# MAP: GENERAL CHEMISTRY: PRINCIPLES, PATTERNS, AND APPLICATIONS (AVERILL)



*Anonymous*
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# Map: General Chemistry: Principles, Patterns, and Applications (Averill)

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# CHAPTER OVERVIEW

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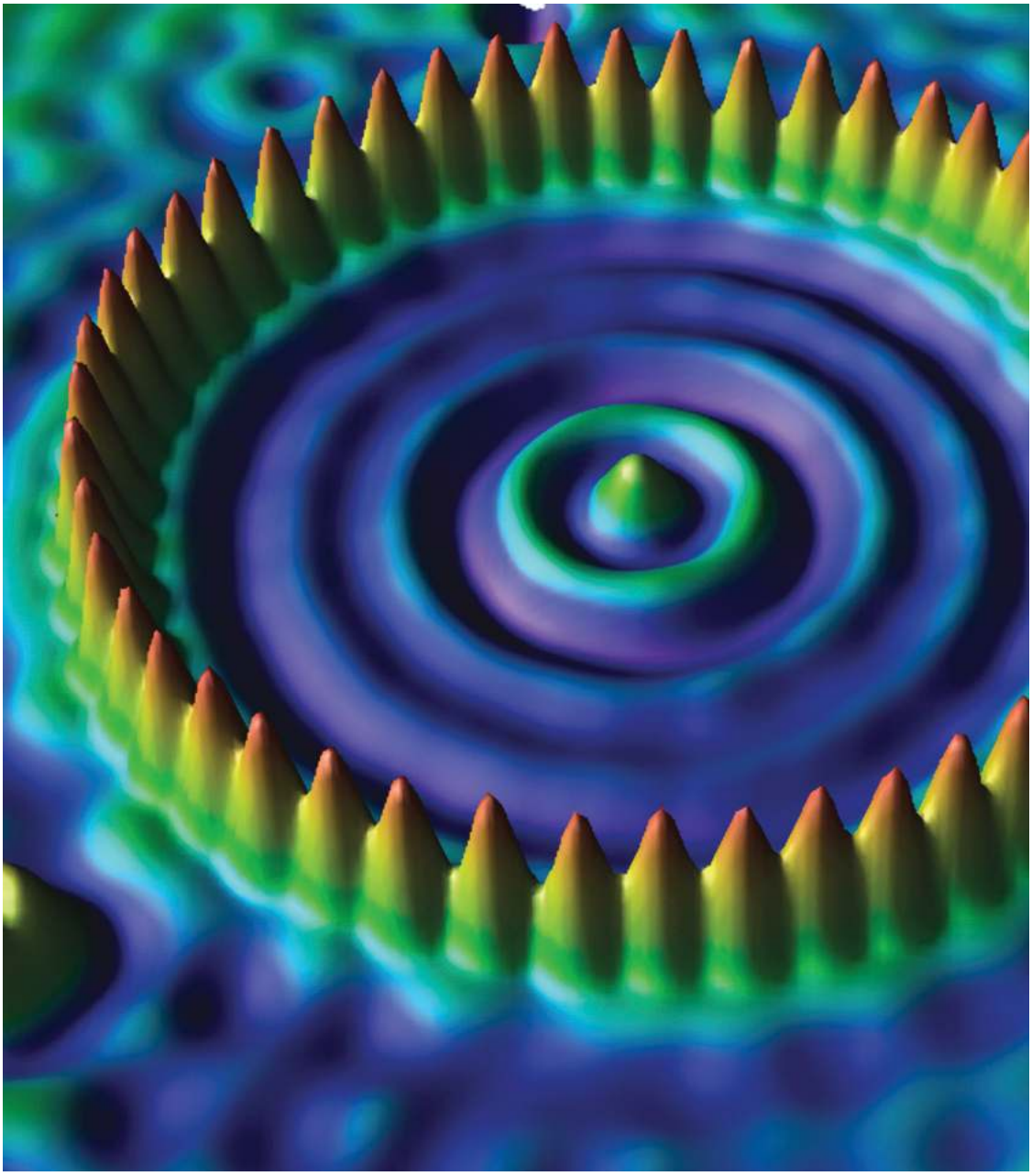

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# 1.1: Introduction

## Introduction to Chemistry

As you begin your study of college chemistry, those of you who do not intend to become professional chemists may well wonder why you need to study chemistry. You will soon discover that a basic understanding of chemistry is useful in a wide range of disciplines and career paths. You will also discover that an understanding of chemistry helps you make informed decisions about many issues that affect you, your community, and your world. A major goal of this text is to demonstrate the importance of chemistry in your daily life and in our collective understanding of both the physical world we occupy and the biological realm of which we are a part. The objectives of this chapter are twofold: (1) to introduce the breadth, the importance, and some of the challenges of modern chemistry and (2) to present some of the fundamental concepts and definitions you will need to understand how chemists think and work.



***An atomic corral for electrons.*** *A corral of 48 iron atoms (yellow-orange) on a smooth copper surface (cyan-purple) confines the electrons on the surface of the copper, producing a pattern of "ripples" in the distribution of the electrons. Scientists assembled the 713-picometer-diameter corral by individually positioning iron atoms with the tip of a scanning tunneling microscope. (Note that 1 picometer is equivalent to* $1 \times 10^{-12}$ *meters.)*

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# 1.2: Chemistry in the Modern World

**Learning Objectives**

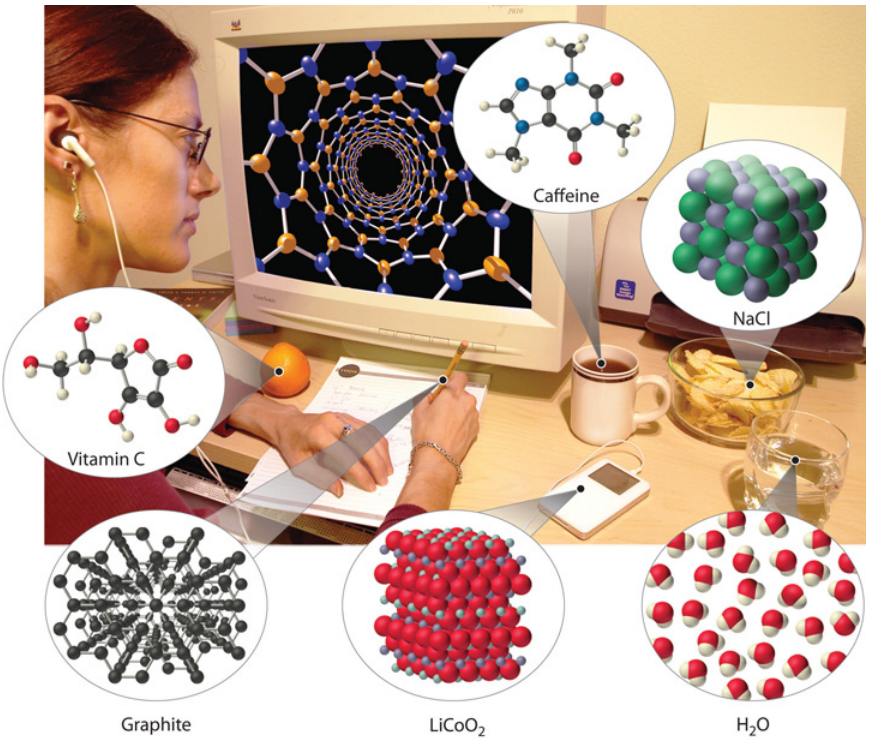
- To recognize the breadth, depth, and scope of chemistry.

**Chemistry** is the study of matter and the changes that material substances undergo. Of all the scientific disciplines, it is perhaps the most extensively connected to other fields of study. Geologists who want to locate new mineral or oil deposits use chemical techniques to analyze and identify rock samples. Oceanographers use chemistry to track ocean currents, determine the flux of nutrients into the sea, and measure the rate of exchange of nutrients between ocean layers. Engineers consider the relationships between the structures and the properties of substances when they specify materials for various uses. Physicists take advantage of the properties of substances to detect new subatomic particles. Astronomers use chemical signatures to determine the age and distance of stars and thus answer questions about how stars form and how old the universe is. The entire subject of environmental science depends on chemistry to explain the origin and impacts of phenomena such as air pollution, ozone layer depletion, and global warming.

The disciplines that focus on living organisms and their interactions with the physical world rely heavily on **biochemistry**, the application of chemistry to the study of biological processes. A living cell contains a large collection of complex molecules that carry out thousands of chemical reactions, including those that are necessary for the cell to reproduce. Biological phenomena such as vision, taste, smell, and movement result from numerous chemical reactions. Fields such as medicine, pharmacology, nutrition, and toxicology focus specifically on how the chemical substances that enter our bodies interact with the chemical components of the body to maintain our health and well-being. For example, in the specialized area of sports medicine, a knowledge of chemistry is needed to understand why muscles get sore after exercise as well as how prolonged exercise produces the euphoric feeling known as “runner’s high.”

Examples of the practical applications of chemistry are everywhere ( Figure 1.2.1 ). Engineers need to understand the chemical properties of the substances when designing biologically compatible implants for joint replacements or designing roads, bridges, buildings, and nuclear reactors that do not collapse because of weakened structural materials such as steel and cement. Archaeology and paleontology rely on chemical techniques to date bones and artifacts and identify their origins. Although law is not normally considered a field related to chemistry, forensic scientists use chemical methods to analyze blood, fibers, and other evidence as they investigate crimes. In particular, DNA matching—comparing biological samples of genetic material to see whether they could have come from the same person—has been used to solve many high-profile criminal cases as well as clear innocent people who have been wrongly accused or convicted. Forensics is a rapidly growing area of applied chemistry. In addition, the proliferation of chemical and biochemical innovations in industry is producing rapid growth in the area of patent law. Ultimately, the dispersal of information in all the fields in which chemistry plays a part requires experts who are able to explain complex chemical issues to the public through television, print journalism, the Internet, and popular books.

Figure 1.2.1 *Chemistry in Everyday Life*



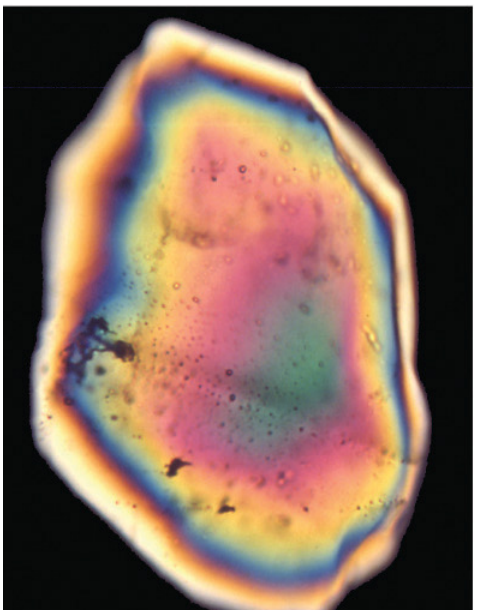

*Although most people do not recognize it, chemistry and chemical compounds are crucial ingredients in almost everything we eat, wear, and use.*

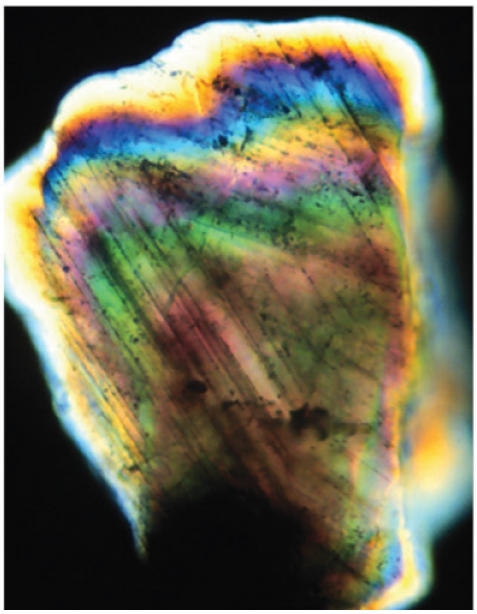
By this point, it shouldn't surprise you to learn that chemistry was essential in explaining a pivotal event in the history of Earth: the disappearance of the dinosaurs. Although dinosaurs ruled Earth for more than 150 million years, fossil evidence suggests that they became extinct rather abruptly approximately 66 million years ago. Proposed explanations for their extinction have ranged from an epidemic caused by some deadly microbe or virus to more gradual phenomena such as massive climate changes. In 1978 Luis Alvarez (a Nobel Prize–winning physicist), the geologist Walter Alvarez (Luis's son), and their coworkers discovered a thin layer of sedimentary rock formed 66 million years ago that contained unusually high concentrations of iridium, a rather rare metal (part (a) in Figure 1.2.2). This layer was deposited at about the time dinosaurs disappeared from the fossil record. Although iridium is very rare in most rocks, accounting for only 0.0000001% of Earth's crust, it is much more abundant in comets and asteroids. Because corresponding samples of rocks at sites in Italy and Denmark contained high iridium concentrations, the Alvarezes suggested that the impact of a large asteroid with Earth led to the extinction of the dinosaurs. When chemists analyzed additional samples of 66-million-year-old sediments from sites around the world, all were found to contain high levels of iridium. In addition, small grains of quartz in most of the iridium-containing layers exhibit microscopic cracks characteristic of high-intensity shock waves (part (b) in Figure 1.2.2). These grains apparently originated from terrestrial rocks at the impact site, which were pulverized on impact and blasted into the upper atmosphere before they settled out all over the world.

Figure 1.2.2 *Evidence for the Asteroid Impact That May Have Caused the Extinction of the Dinosaurs*




(a)

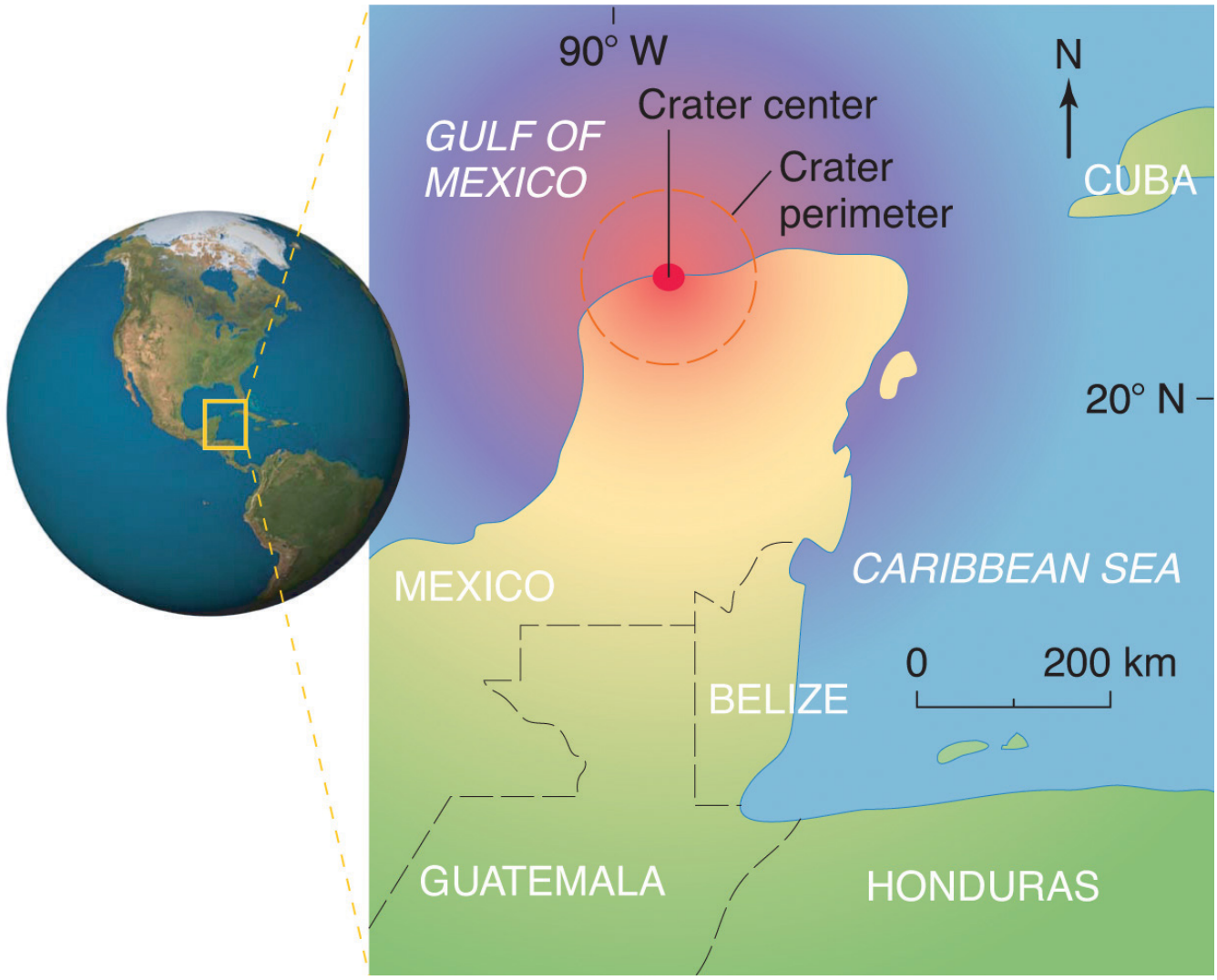




[redacted] *front of a rock formation in Italy that shows the thin white layer of iridium-rich clay deposited at the time the dinosaurs became extinct. The concentration of iridium is 30 times higher in this layer than in the rocks immediately above and below it. There are no significant differences between the clay layer and the surrounding rocks in the concentrations of any of the 28 other elements examined. (b) Microphotographs of an unshocked quartz grain (left) and a quartz grain from the iridium-rich layer exhibiting microscopic cracks resulting from shock (right).*

Scientists calculate that a collision of Earth with a stony asteroid about 10 kilometers (6 miles) in diameter, traveling at 25 kilometers per second (about 56,000 miles per hour), would almost instantaneously release energy equivalent to the explosion of about 100 million megatons of TNT (trinitrotoluene). This is more energy than that stored in the entire nuclear arsenal of the world. The energy released by such an impact would set fire to vast areas of forest, and the smoke from the fires and the dust created by the impact would block the sunlight for months or years, eventually killing virtually all green plants and most organisms that depend on them. This could explain why about 70% of *all* species—not just dinosaurs—disappeared at the same time. Scientists also calculate that this impact would form a crater at least 125 kilometers (78 miles) in diameter. Recently, satellite images from a Space Shuttle mission confirmed that a huge asteroid or comet crashed into Earth's surface across the Yucatan's northern tip in the Gulf of Mexico 65 million years ago, leaving a partially submerged crater 180 kilometers (112 miles) in diameter (Figure 1.2.3 ). Thus simple chemical measurements of the abundance of one element in rocks led to a new and dramatic explanation for the extinction of the dinosaurs. Though still controversial, this explanation is supported by additional evidence, much of it chemical.

Figure 1.2.3 *Asteroid Impact*




*The location of the asteroid impact crater near what is now the tip of the Yucatan Peninsula in Mexico.*

This is only one example of how chemistry has been applied to an important scientific problem. Other chemical applications and explanations that we will discuss in this text include how astronomers determine the distance of galaxies and how fish can survive in subfreezing water under polar ice sheets. We will also consider ways in which chemistry affects our daily lives: the addition of iodine to table salt; the development of more effective drugs to treat diseases such as cancer, AIDS (acquired immunodeficiency syndrome), and arthritis; the retooling of industry to use nonchlorine-containing refrigerants, propellants, and other chemicals to preserve Earth's ozone layer; the use of modern materials in engineering; current efforts to control the problems of acid rain and global warming; and the awareness that our bodies require small amounts of some chemical substances that are toxic when ingested in larger doses. By the time you finish this text, you will be able to discuss these kinds of topics knowledgeably, either as a beginning scientist who intends to spend your career studying such problems or as an informed observer who is able to participate in public debates that will certainly arise as society grapples with scientific issues.

## Summary

**Chemistry** is the study of matter and the changes material substances undergo. It is essential for understanding much of the natural world and central to many other scientific disciplines, including astronomy, geology, paleontology, biology, and medicine.

## KEY TAKEAWAY

- An understanding of chemistry is essential for understanding much of the natural world and is central to many other disciplines.

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# 1.3: The Scientific Method

**Learning Objectives**

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.3.1).

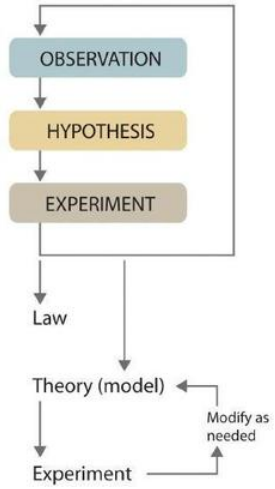



Figure 1.3.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

Observations can be qualitative or quantitative. Qualitative observations describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. Quantitative observations are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 °C, and 35.9 grams of table salt—whose chemical name is sodium chloride—dissolve in 100 grams of water at 20 °C. An example of a quantitative observation was the initial observation leading to the modern theory of the dinosaurs' extinction: iridium concentrations in sediments dating to 66 million years ago were found to be 20–160 times higher than normal. The development of this theory is a good exemplar of the scientific method in action (see Figure 1.3.2 below).

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a **hypothesis**, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

1. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
2. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists collected additional data that either support or refute it.

After a hypothesis has been formed, scientists conduct experiments to test its validity. **Experiments** are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes. For example, in the dinosaur extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed

and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a **law**, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the Law of Definite Proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. Some solid compounds do not strictly obey the law of definite proportions. The law of definite proportions should seem obvious—we would expect the composition of sodium chloride to be consistent—but the head of the US Patent Office did not accept it as a fact until the early 20th century.

Whereas a law states only what happens, a **theory** attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 1.3.2 summarizes the application of the scientific method in this case.

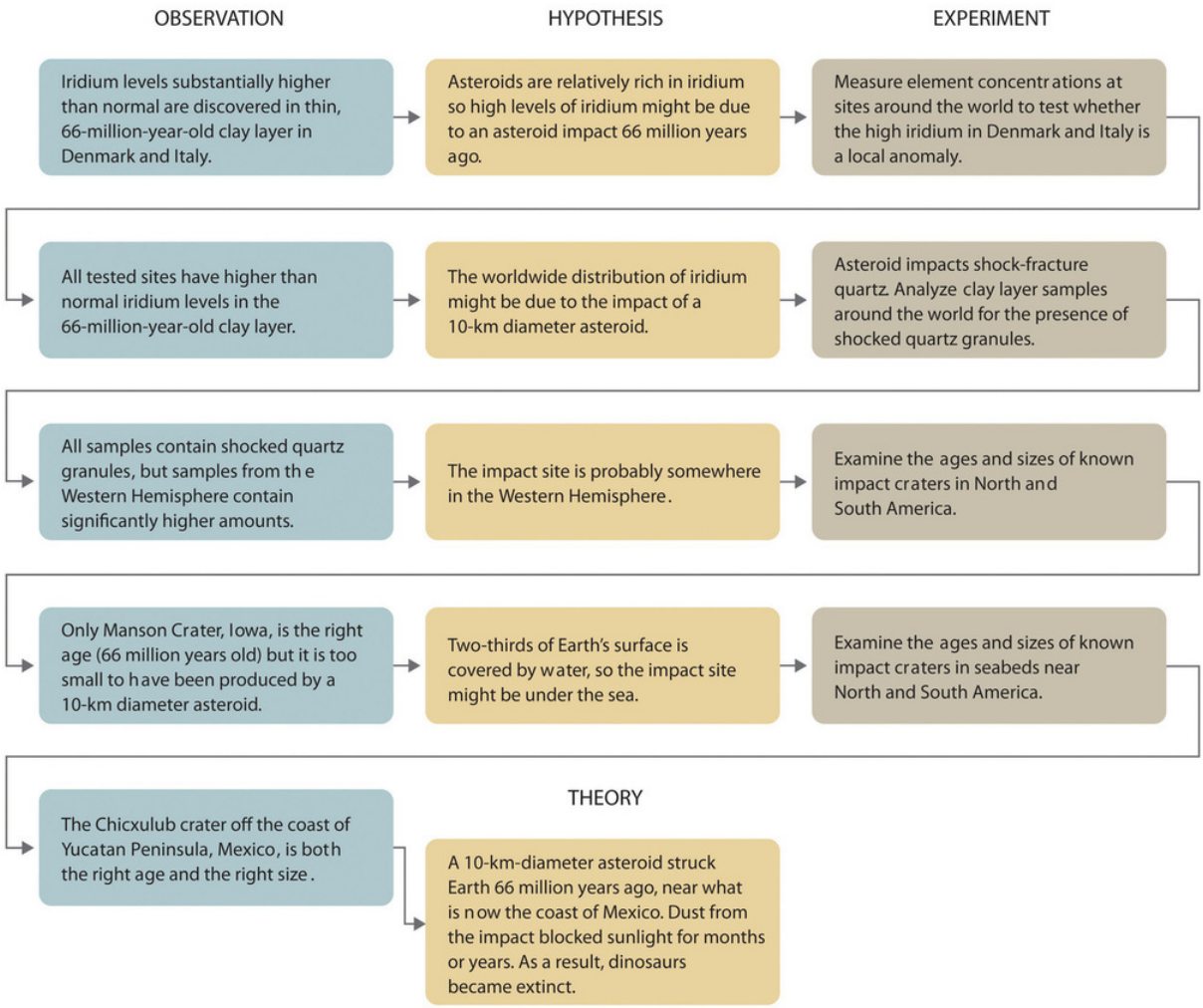



Figure 1.3.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

### Example 1.3.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
d. When 10 g of ice were added to 100 mL of water at 25 °C, the temperature of the water decreased to 15.5 °C after the ice melted.
e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

**Given**: components of the scientific method

**Asked for**: statement classification

**Strategy:** Refer to the definitions in this section to determine which category best describes each statement.

**Solution**

a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
b. This is a possible explanation for the origin of birds, so it is a hypothesis.
c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
d. The temperature is measured before and after a change is made in a system, so these are quantitative observations.
e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

### Exercise 1.3.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.
d. Michael Jordan is the greatest pure shooter ever to play professional basketball.
e. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
f. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

**Answer a**

experiment

**Answer b**

law

**Answer c**

theory

**Answer d**

hypothesis

**Answer e**

qualitative observation

**Answer f**

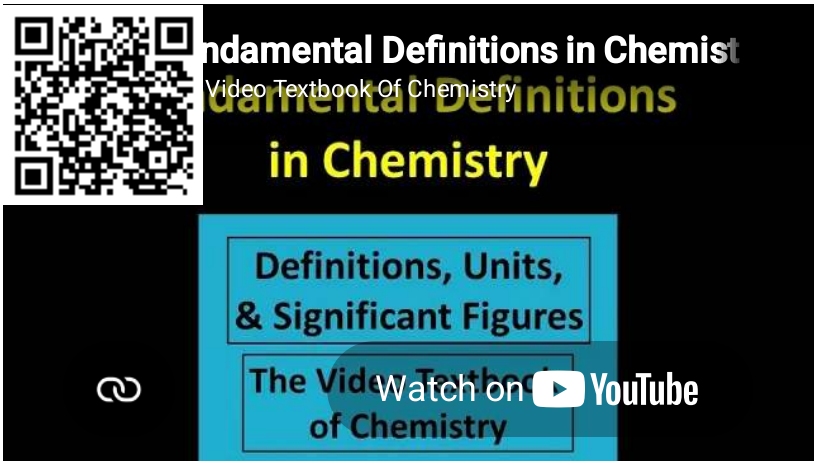
quantitative observation

Because scientists can enter the cycle shown in Figure 1.3.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

It is important to remember that scientists have a tendency to formulate hypotheses in familiar terms simply because it is difficult to propose something that has never been encountered or imagined before. As a result, scientists sometimes discount or overlook unexpected findings that disagree with the basic assumptions behind the hypothesis or theory being tested. Fortunately, truly important findings are immediately subject to independent verification by scientists in other laboratories, so science is a self-correcting discipline. When the Alvarezes originally suggested that an extraterrestrial impact caused the extinction of the dinosaurs, the response was almost universal skepticism and scorn. In only 20 years, however, the persuasive nature of the evidence overcame the skepticism of many scientists, and their initial hypothesis has now evolved into a theory that has revolutionized paleontology and geology.

## Summary

Chemists expand their knowledge by making observations, carrying out experiments, and testing hypotheses to develop laws to summarize their results and theories to explain them. In doing so, they are using the scientific method.




Fundamental Definitions in Chemistry: https://youtu.be/SBwjbkFNkdw

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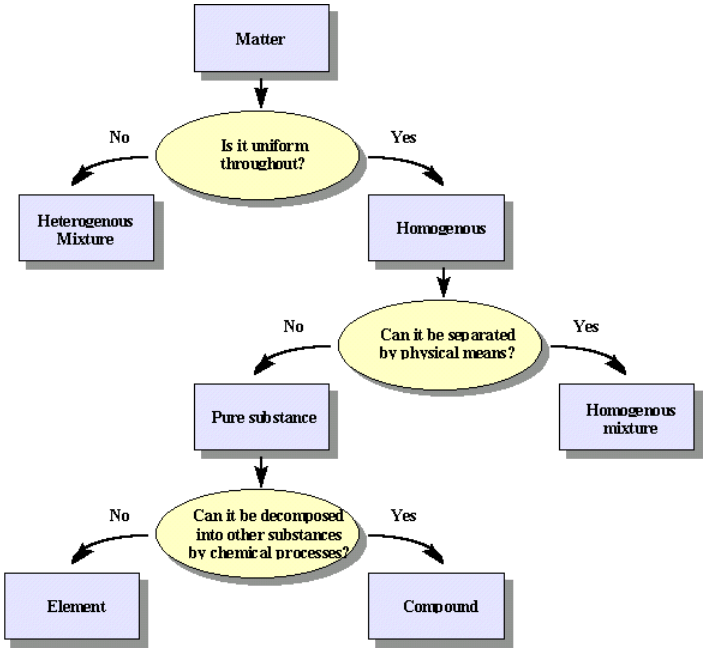
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# 1.4: A Description of Matter

Pure substances have an invariable composition and are composed of either **elements** or **compounds**.

- **Elements:** *"Substances which cannot be decomposed into simpler substances by chemical means"*.
- **Compounds**: ***Can*** be decomposed into two or more elements.



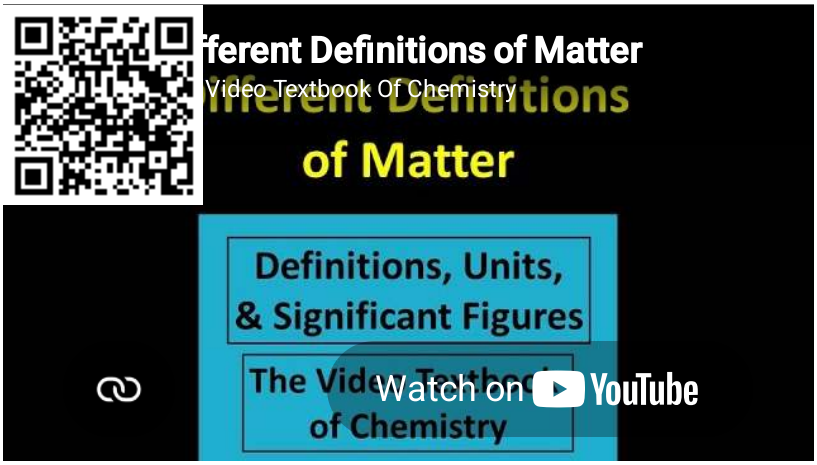

## Elements

Elements are the basic substances out of which all matter is composed.

- Everything in the world is made up from only **109** different elements.
- 90% of the human body is composed of only three elements: Oxygen, Carbon and Hydrogen

Elements are known by common names as well as by their **abbreviations**. These consisting of one or two letters, with the first one capitalized. These abbreviations are derived from English or foreign words (e.g. Latin, German).

| Element | Abbreviation |
|---|---|
| Carbon | C |
| Fluorine | F |
| Hydrogen | H |
| Iodine | I |
| Nitrogen | N |
| Oxygen | O |
| Phosphorus | P |
| Sulfur | S |
| Aluminum | Al |
| Barium | Ba |
| Calcium | Ca |
| Chlorine | Cl |
| Helium | He |
| Magnesium | Mg |
| Platinum | Pt |
| Silicon | Si |
| Copper | Cu (from cuprum) |
| Iron | Fe (from ferrum) |
| Lead | Pb (from plumbum) |
| Mercury | Hg (from hydrargyrum) |
| Potassium | K (from kalium) |
| Silver | Ag (from argentum) |
| Sodium | Na (from natrium) |
| Tin | Sn (from stannum) |




Different Definitions of Matter: https://youtu.be/qi_qLHc8wLk

## Compounds

Compounds are substances of two or more elements **united chemically in definite proportions by mass**. For example, pure water is composed of the elements hydrogen (H) and oxygen (O) at the **defined ratio** of 11 % hydrogen and 89 % oxygen by **mass**.

The observation that the elemental composition of a pure compound is always the same is known as the **law of constant composition** (or **the law of definite proportions**). It is credited to the French chemist Joseph Louis Proust (1754-1826).

## Contributors and Attributions

Mike Blaber (Florida State University)

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# 1.5: A Brief History of Chemistry

**Learning Objectives**

- To understand the development of the atomic model.

It was not until the era of the ancient Greeks that we have any record of how people tried to explain the chemical changes they observed and used. At that time, natural objects were thought to consist of only four basic elements: earth, air, fire, and water. Then, in the fourth century BC, two Greek philosophers, Democritus and Leucippus, suggested that matter was not infinitely divisible into smaller particles but instead consisted of fundamental, indivisible particles called **atoms**. Unfortunately, these early philosophers did not have the technology to test their hypothesis. They would have been unlikely to do so in any case because the ancient Greeks did not conduct experiments or use the scientific method. They believed that the nature of the universe could be discovered by rational thought alone.

Over the next two millennia, *alchemists*, who engaged in a form of chemistry and speculative philosophy during the Middle Ages and Renaissance, achieved many advances in chemistry. Their major goal was to convert certain elements into others by a process they called **transmutation** (Figure 1.5.1 ). In particular, alchemists wanted to find a way to transform cheaper metals into gold. Although most alchemists did not approach chemistry systematically and many appear to have been outright frauds, alchemists in China, the Arab kingdoms, and medieval Europe made major contributions, including the discovery of elements such as quicksilver (mercury) and the preparation of several strong acids.

Figure 1.5.1 *An Alchemist at Work*




*Alchemy was a form of chemistry that flourished during the Middle Ages and Renaissance. Although some alchemists were frauds, others made major contributions, including the discovery of several elements and the preparation of strong acids.*

## Modern Chemistry

The 16th and 17th centuries saw the beginnings of what we now recognize as modern chemistry. During this period, great advances were made in *metallurgy*, the extraction of metals from ores, and the first systematic quantitative experiments were carried out. In 1661, the Englishman Robert Boyle (1627–91) published *The Sceptical Chymist*, which described the relationship between the pressure and the volume of air. More important, Boyle defined an element as a substance that cannot be broken down into two or more simpler substances by chemical means. This led to the identification of a large number of elements, many of which were metals. Ironically, Boyle himself never thought that metals were elements.

In the 18th century, the English clergyman Joseph Priestley (1733–1804) discovered oxygen gas and found that many carbon-containing materials burn vigorously in an oxygen atmosphere, a process called **combustion**. Priestley also discovered that the gas produced by fermenting beer, which we now know to be carbon dioxide, is the same as one of the gaseous products of combustion. Priestley's studies of this gas did not continue as he would have liked, however. After he fell into a vat of fermenting beer, brewers prohibited him from working in their factories. Although Priestley did not understand its identity, he found that carbon dioxide dissolved in water to produce seltzer water. In essence, he may be considered the founder of the multibillion-dollar carbonated soft drink industry.

### Joseph Priestley (1733–1804)

Priestley was a political theorist and a leading Unitarian minister. He was appointed to Warrington Academy in Lancashire, England, where he developed new courses on history, science, and the arts. During visits to London, Priestley met the leading men of science, including Benjamin Franklin, who encouraged Priestley's interest in electricity. Priestley's work on gases began while he was living next to a brewery in Leeds, where he noticed "fixed air" bubbling out of vats of fermenting beer and ale. His scientific discoveries included the relationship between electricity and chemical change, 10 new "airs," and observations that led to the discovery of photosynthesis. Due to his support for the principles of the French Revolution, Priestley's house, library, and laboratory were destroyed by a mob in 1791. He and his wife emigrated to the United States in 1794 to join their three sons, who had previously emigrated to Pennsylvania. Priestley never returned to England and died in his new home in Pennsylvania.

Despite the pioneering studies of Priestley and others, a clear understanding of combustion remained elusive. In the late 18th century, however, the French scientist Antoine Lavoisier (1743–94) showed that combustion is the reaction of a carbon-containing substance with oxygen to form carbon dioxide and water and that life depends on a similar reaction, which today we call *respiration*. Lavoisier also wrote the first modern chemistry text and is widely regarded as the father of modern chemistry. His most important contribution was the **law of conservation of mass**, which states that in any chemical reaction, the mass of the substances that react equals the mass of the products that are formed. That is, in a chemical reaction, mass is neither lost nor destroyed. Unfortunately, Lavoisier invested in a private corporation that collected taxes for the Crown, and royal tax collectors were not popular during the French Revolution. He was executed on the guillotine at age 51, prematurely terminating his contributions to chemistry.

## The Atomic Theory of Matter

In 1803, the English schoolteacher John Dalton (1766–1844) expanded Proust's development of the **law of definite proportions** (Section 1.2) and Lavoisier's findings on the conservation of mass in chemical reactions to propose that elements consist of indivisible particles that he called *atoms* (taking the term from Democritus and Leucippus). Dalton's *atomic theory of matter* contains four fundamental hypotheses:

1. All matter is composed of tiny indivisible particles called atoms.
2. All atoms of an element are identical in mass and chemical properties, whereas atoms of different elements differ in mass and fundamental chemical properties.
3. A chemical compound is a substance that always contains the same atoms in the same ratio.
4. In chemical reactions, atoms from one or more compounds or elements redistribute or rearrange in relation to other atoms to form one or more new compounds. *Atoms themselves do not undergo a change of identity in chemical reactions.*

This last hypothesis suggested that the alchemists' goal of transmuting other elements to gold was impossible, at least through chemical reactions. We now know that Dalton's atomic theory is essentially correct, with four minor modifications:

1. Not all atoms of an element must have precisely the same mass.

2. Atoms of one element can be transformed into another through nuclear reactions.
3. The compositions of many solid compounds are somewhat variable.
4. Under certain circumstances, some atoms can be divided (split into smaller particles).

These modifications illustrate the effectiveness of the scientific method; later experiments and observations were used to refine Dalton's original theory.

## The Law of Multiple Proportions

Despite the clarity of his thinking, Dalton could not use his theory to determine the elemental compositions of chemical compounds because he had no reliable scale of atomic masses; that is, he did not know the relative masses of elements such as carbon and oxygen. For example, he knew that the gas we now call carbon monoxide contained carbon and oxygen in the ratio 1:1.33 by mass, and a second compound, the gas we call carbon dioxide, contained carbon and oxygen in the ratio 1:2.66 by mass. Because 2.66/1.33 = 2.00, the second compound contained twice as many oxygen atoms per carbon atom as did the first. But what was the correct formula for each compound? If the first compound consisted of particles that contain one carbon atom and one oxygen atom, the second must consist of particles that contain one carbon atom and two oxygen atoms. If the first compound had two carbon atoms and one oxygen atom, the second must have two carbon atoms and two oxygen atoms. If the first had one carbon atom and two oxygen atoms, the second would have one carbon atom and four oxygen atoms, and so forth. Dalton had no way to distinguish among these or more complicated alternatives. However, these data led to a general statement that is now known as the **law of multiple proportions**: when two elements form a series of compounds, the ratios of the masses of the second element that are present per gram of the first element can almost always be expressed as the ratios of integers. (The same law holds for mass ratios of compounds forming a series that contains more than two elements.) Example 4 shows how the law of multiple proportions can be applied to determine the identity of a compound.

### Example 1.5.1

A chemist is studying a series of simple compounds of carbon and hydrogen. The following table lists the masses of hydrogen that combine with 1 g of carbon to form each compound.

| Compound | Mass of Hydrogen (g) |
|---|---|
| *A* | 0.0839 |
| *B* | 0.1678 |
| *C* | 0.2520 |
| *D* | |

1. Determine whether these data follow the law of multiple proportions.
2. Calculate the mass of hydrogen that would combine with 1 g of carbon to form *D*, the fourth compound in the series.

**Given:** mass of hydrogen per gram of carbon for three compounds

**Asked for:**

1. ratios of masses of hydrogen to carbon
2. mass of hydrogen per gram of carbon for fourth compound in series

**Strategy:**

**A** Select the lowest mass to use as the denominator and then calculate the ratio of each of the other masses to that mass. Include other ratios if appropriate.

**B** If the ratios are small whole integers, the data follow the law of multiple proportions.

**C** Decide whether the ratios form a numerical series. If so, then determine the next member of that series and predict the ratio corresponding to the next compound in the series.

**D** Use proportions to calculate the mass of hydrogen per gram of carbon in that compound.

**Solution**

**A** Compound *A* has the lowest mass of hydrogen, so we use it as the denominator. The ratios of the remaining masses of hydrogen, *B* and *C*, that combine with 1 g of carbon are as follows:

CA=0.2520 g0.0839 g=3.00=31BA=0.1678 g0.0839 g=2.00=21CB=0.2520 g0.1678 g=1.502≈32

**B** The ratios of the masses of hydrogen that combine with 1 g of carbon are indeed composed of small whole integers (3/1, 2/1, 3/2), as predicted by the law of multiple proportions.

**C** The ratios *B*/*A* and *C*/*A* form the series 2/1, 3/1, so the next member of the series should be *D*/*A* = 4/1.

**D** Thus, if compound *D* exists, it would be formed by combining 4 × 0.0839 g = 0.336 g of hydrogen with 1 g of carbon. Such a compound does exist; it is *methane*, the major constituent of natural gas.

## ? Exercise 1.5.1

Four compounds containing only sulfur and fluorine are known. The following table lists the masses of fluorine that combine with 1 g of sulfur to form each compound.

| Compound | Mass of Fluorine (g) |
|---|---|
| *A* | 3.54 |
| *B* | 2.96 |
| *C* | 2.36 |
| *D* | 0.59 |

1. Determine the ratios of the masses of fluorine that combine with 1 g of sulfur in these compounds. Are these data consistent with the law of multiple proportions?
2. Calculate the mass of fluorine that would combine with 1 g of sulfur to form the next two compounds in the series: *E* and *F*.

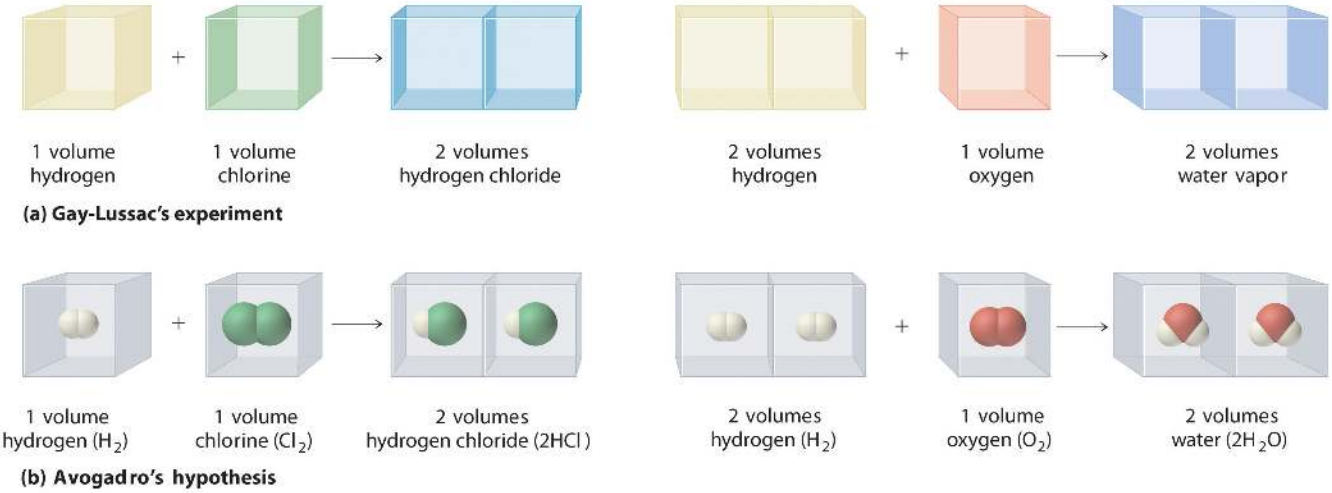
**Answer**

1. *A*/*D* = 6.0 or 6/1; *B*/*D* ≈ 5.0, or 5/1; *C*/*D* = 4.0, or 4/1; yes
2. Ratios of 3.0 and 2.0 give 1.8 g and 1.2 g of fluorine/gram of sulfur, respectively. (Neither of these compounds is yet known.)

## Avogadro's Hypothesis

In a further attempt to establish the formulas of chemical compounds, the French chemist Joseph Gay-Lussac (1778–1850) carried out a series of experiments using volume measurements. Under conditions of constant temperature and pressure, he carefully measured the volumes of gases that reacted to make a given chemical compound, together with the volumes of the products if they were gases. Gay-Lussac found, for example, that one volume of chlorine gas always reacted with one volume of hydrogen gas to produce two volumes of hydrogen chloride gas. Similarly, one volume of oxygen gas always reacted with two volumes of hydrogen gas to produce two volumes of water vapor (part (a) in Figure 1.5.2).

Figure 1.5.2 *Gay-Lussac's Experiments with Chlorine Gas and Hydrogen Gas*



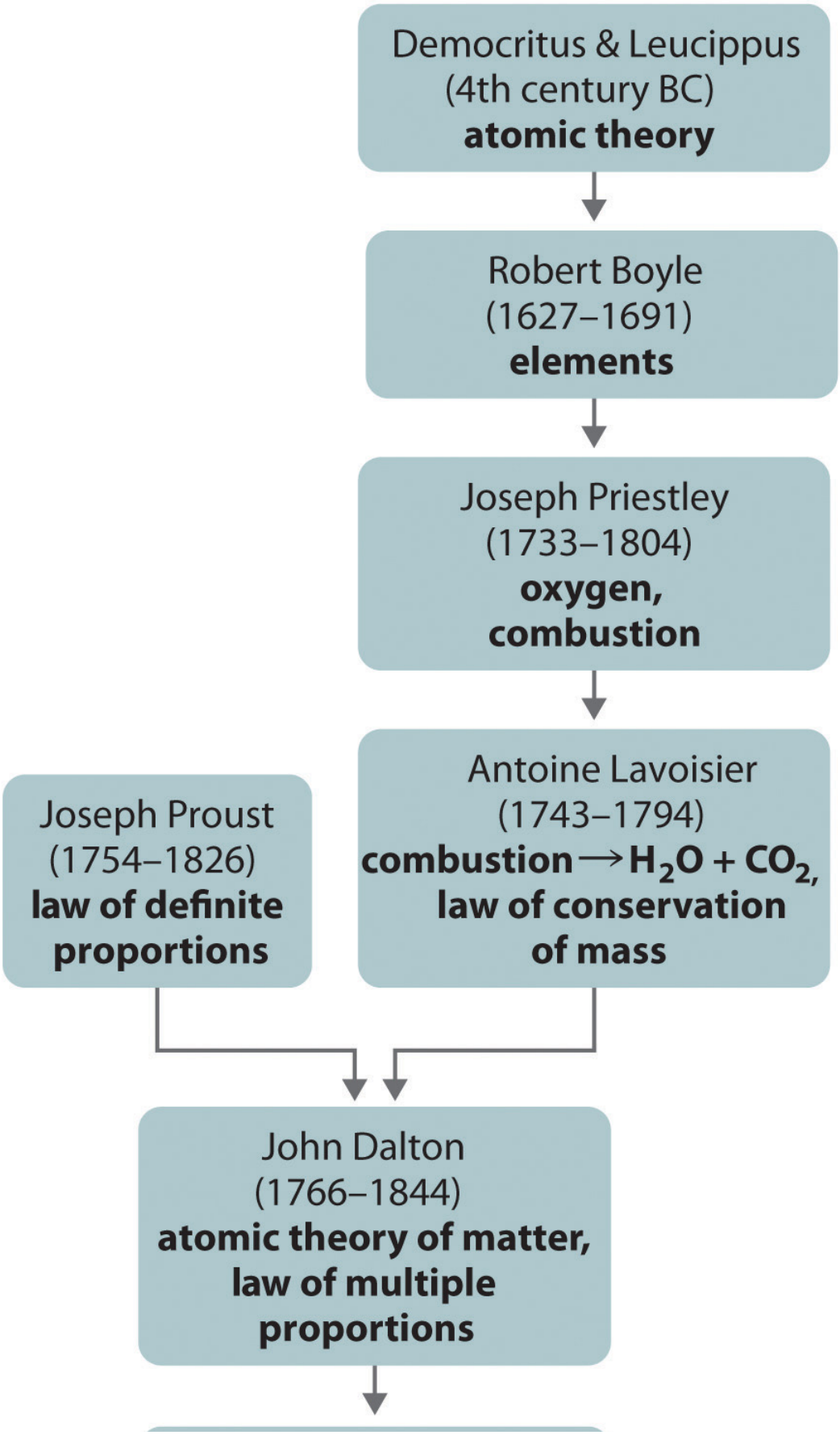

*(a) One volume of chlorine gas reacted with one volume of hydrogen gas to produce two volumes of hydrogen chloride gas, and one volume of oxygen gas reacted with two volumes of hydrogen gas to produce two volumes of water vapor. (b) A summary of Avogadro's hypothesis, which interpreted Gay-Lussac's results in terms of atoms. Note that the simplest way for two molecules of hydrogen chloride to be produced is if hydrogen and chlorine each consist of molecules that contain two atoms of the element.*

Gay-Lussac's results did not by themselves reveal the formulas for hydrogen chloride and water. The Italian chemist Amadeo Avogadro (1776–1856) developed the key insight that led to the exact formulas. He proposed that when gases are measured at the same temperature and pressure, *equal volumes of different gases contain equal numbers of gas particles*. *Avogadro's hypothesis*, which explained Gay-Lussac's results, is summarized here and in part (b) in Figure 1.5.2:

$$one volume (or particle) of hydrogen + one volume (or particle) of chlorine \rightarrow two volumes (or particles) of hydrogen chloride$$

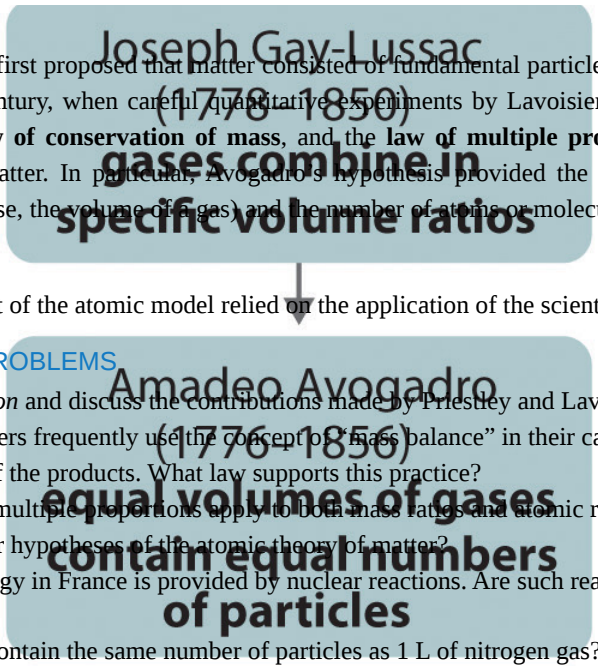
If Dalton's theory of atoms was correct, then each particle of hydrogen or chlorine had to contain *at least two atoms* of hydrogen or chlorine because two particles of hydrogen chloride were produced. The simplest—but not the only—explanation was that hydrogen and chlorine contained two atoms each (i.e., they were *diatomic*) and that hydrogen chloride contained one atom each of hydrogen and chlorine. Applying this reasoning to Gay-Lussac's results with hydrogen and oxygen leads to the conclusion that water contains two hydrogen atoms per oxygen atom. Unfortunately, because no data supported Avogadro's hypothesis that equal volumes of gases contained equal numbers of particles, his explanations and formulas for simple compounds were not generally accepted for more than 50 years. Dalton and many others continued to believe that water particles contained one hydrogen atom and one oxygen atom, rather than two hydrogen atoms and one oxygen atom. The historical development of the concept of the atom is summarized in Figure 1.5.3.

Figure 1.5.3 *A Summary of the Historical Development of the Concept of the Atom*


Democritus & Leucippus
(4th century BC)
atomic theory
Robert Boyle
(1627–1691)
elements
Joseph Priestley
(1733–1804)
oxygen,
combustion
Antoine Lavoisier
(1743–1794)
combustion → $H_2O + CO_2$,
law of conservation
of mass
Joseph Proust
(1754–1826)
law of definite
proportions
John Dalton
(1766–1844)
atomic theory of matter,
law of multiple
proportions

## Summary

The ancient Greeks first proposed that matter consisted of fundamental particles called **atoms**. Chemistry took its present scientific form in the 18th century, when careful quantitative experiments by Lavoisier, Proust, and Dalton resulted in the law of definite proportions, the **law of conservation of mass**, and the **law of multiple proportions**, which laid the groundwork for Dalton's atomic theory of matter. In particular, Avogadro's hypothesis provided the first link between the macroscopic properties of a substance (in this case, the volume of a gas) and the number of atoms or molecules present.




## KEY TAKEAWAY

- The development of the atomic model relied on the application of the scientific method over several centuries.

## CONCEPTUAL PROBLEMS

1. Define *combustion* and discuss the contributions made by Priestley and Lavoisier toward understanding a combustion reaction.
2. Chemical engineers frequently use the concept of "mass balance" in their calculations, in which the mass of the reactants must equal the mass of the products. What law supports this practice?
3. Does the law of multiple proportions apply to both mass ratios and atomic ratios? Why or why not?
4. What are the four hypotheses of the atomic theory of matter?
5. Much of the energy in France is provided by nuclear reactions. Are such reactions consistent with Dalton's hypotheses? Why or why not?
6. Does 1 L of air contain the same number of particles as 1 L of nitrogen gas? Explain your answer.

## NUMERICAL PROBLEMS

*Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9) before proceeding to the Numerical Problems.*

1. One of the minerals found in soil has an Al:Si:O atomic ratio of 0.2:0.2:0.5. Is this consistent with the law of multiple proportions? Why or why not? Is the ratio of elements consistent with Dalton's atomic theory of matter?
2. Nitrogen and oxygen react to form three different compounds that contain 0.571 g, 1.143 g, and 2.285 g of oxygen/gram of nitrogen, respectively. Is this consistent with the law of multiple proportions? Explain your answer.
3. Three binary compounds of vanadium and oxygen are known. The following table gives the masses of oxygen that combine with 10.00 g of vanadium to form each compound.

| Compound | Mass of Oxygen (g) |
|---|---|
| *A* | 4.71 |
| *B* | 6.27 |
| *C* | |

   1. Determine the ratio of the masses of oxygen that combine with 3.14 g of vanadium in compounds *A* and *B*.
   2. Predict the mass of oxygen that would combine with 3.14 g of vanadium to form the third compound in the series.
4. Three compounds containing titanium, magnesium, and oxygen are known. The following table gives the masses of titanium and magnesium that react with 5.00 g of oxygen to form each compound.

| Compound | Mass of Titanium (g) | Mass of Magnesium (g) |
|---|---|---|
| *A* | 4.99 | 2.53 |
| *B* | 3.74 | 3.80 |
| *C* | | |

   1. Determine the ratios of the masses of titanium and magnesium that combine with 5.00 g of oxygen in these compounds.
   2. Predict the masses of titanium and magnesium that would combine with 5.00 g of oxygen to form another possible compound in the series: *C*.

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# 1.6: The Atom

**Learning Objectives**

- To become familiar with the components and structure of the atom.

To date, about 115 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components.

Atoms consist of **electrons**, **protons**, and **neutrons**.This is an oversimplification that ignores the other subatomic particles that have been discovered, but it is sufficient for our discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 1.6.1 , which illustrates three important points.

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. We usually assign *relative* charges of −1 and +1 to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute by far the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom's structure is one of the greatest detective stories in the history of science.

Table 1.6.1 Properties of Subatomic Particles*

| Particle | Mass (g) | Atomic Mass (amu) | Electrical Charge (coulombs) | Relative Charge |
|---|---|---|---|---|
| electron | $9.109 \times 10^{-28}$ | 0.0005486 | $-1.602 \times 10^{-19}$ | −1 |
| proton | $1.673 \times 10^{-24}$ | 1.007276 | $+1.602 \times 10^{-19}$ | +1 |
| neutron | $1.675 \times 10^{-24}$ | 1.008665 | 0 | 0 |

* For a review of using scientific notation and units of measurement, see Essential Skills 1 (Section 1.9).

## The Electron

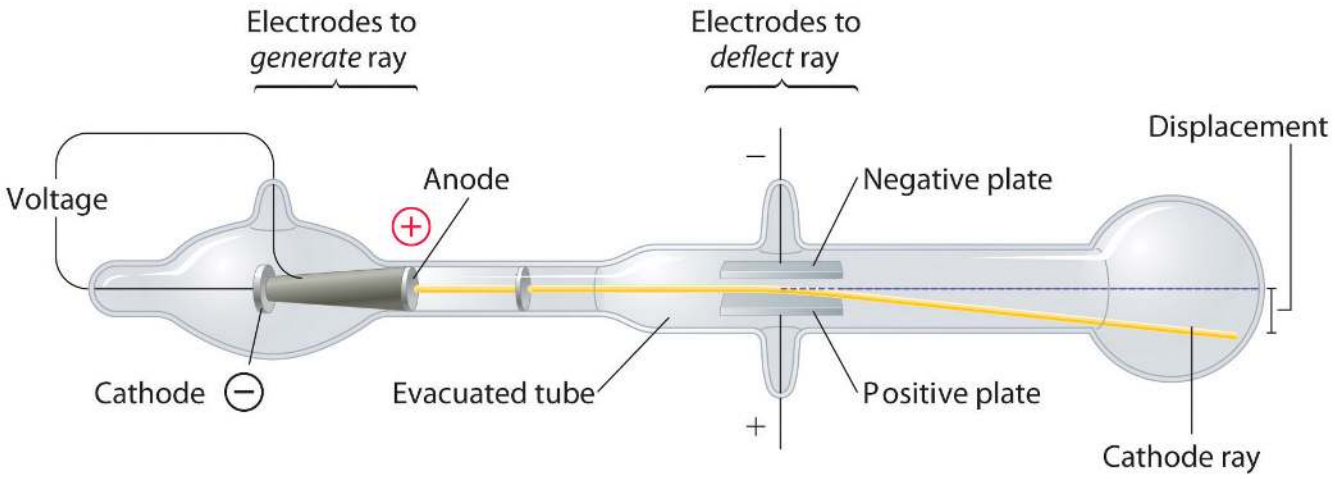
Figure 1.6.1 *A Gas Discharge Tube Producing Cathode Rays (CC-By_SA Wikipeida, Svk Mary)*



*When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light.*

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure 1.6.1 ). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the *cathode*, or negatively charged electrode; hence this form of energy was called *cathode rays*. In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the ultimate form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 1.6.2). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the *mass-to-charge ratio* of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; we now call these particles **electrons**. Most important for chemistry, Thomson found that the mass-to-charge ratio of cathode rays was independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

Figure 1.6.2 *Deflection of Cathode Rays by an Electric Field*




*As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged.*

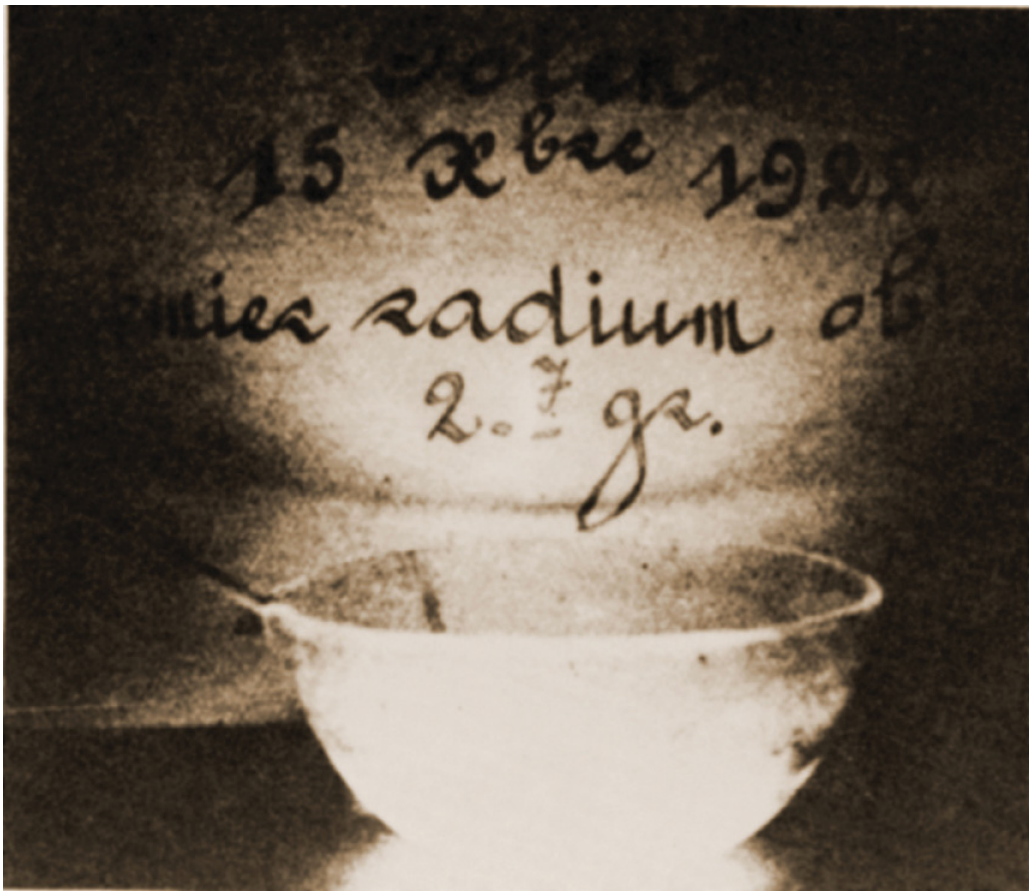
Subsequently, the American scientist Robert Millikan (1868–1953) carried out a series of experiments using electrically charged oil droplets, which allowed him to calculate the charge on a single electron. With this information and Thomson's mass-to-charge ratio, Millikan determined the mass of an electron:

$dfracmasschargeXcharge = mass$

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy.

## Radioactivity

The second line of investigation began in 1896, when the French physicist Henri Becquerel (1852–1908) discovered that certain minerals, such as uranium salts, emitted a new form of energy. Becquerel's work was greatly extended by Marie Curie (1867–1934) and her husband, Pierre (1854–1906); all three shared the Nobel Prize in Physics in 1903. Marie Curie coined the term **radioactivity** (from the Latin *radius*, meaning "ray") to describe the emission of energy rays by matter. She found that one particular uranium ore, pitchblende, was substantially more radioactive than most, which suggested that it contained one or more highly radioactive impurities. Starting with several tons of pitchblende, the Curies isolated two new radioactive elements after months of work: polonium, which was named for Marie's native Poland, and radium, which was named for its intense radioactivity. Pierre Curie carried a vial of radium in his coat pocket to demonstrate its greenish glow, a habit that caused him to become ill from radiation poisoning well before he was run over by a horse-drawn wagon and killed instantly in 1906. Marie Curie, in turn, died of what was almost certainly radiation poisoning.

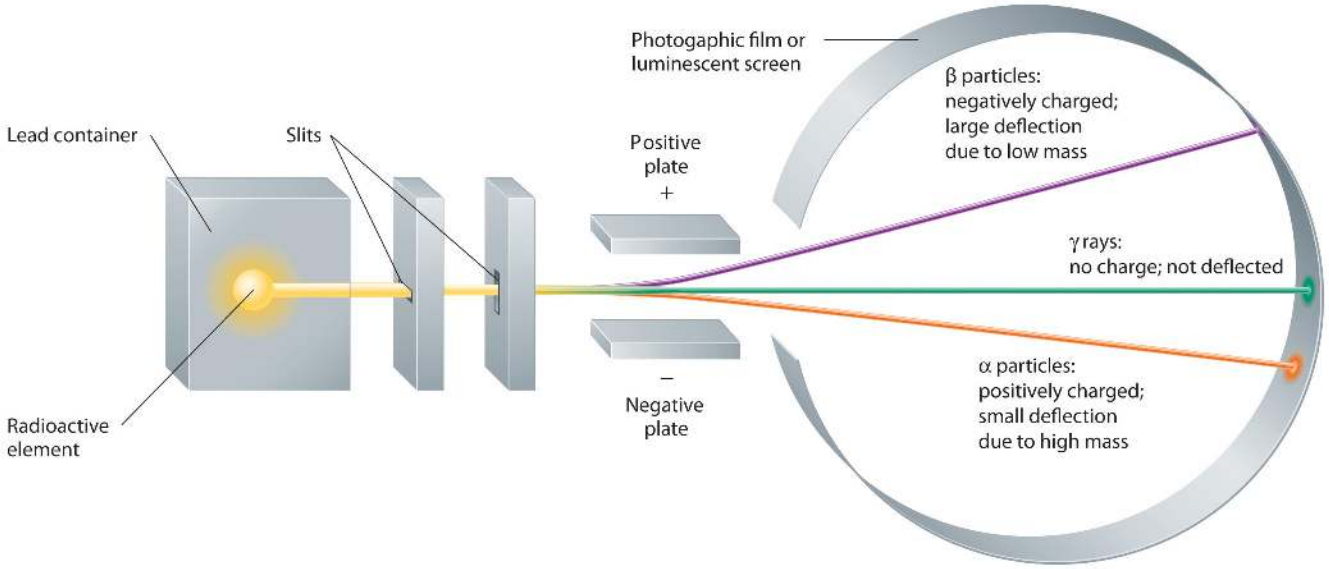



***Radium bromide illuminated by its own radioactive glow.*** *This 1922 photo was taken in the dark in the Curie laboratory.*

Building on the Curies' work, the British physicist Ernest Rutherford (1871–1937) performed decisive experiments that led to the modern view of the structure of the atom. While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances *α particles*. Rutherford also showed that the particles in the second type of radiation, *β particles*, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. A third type of radiation, *γ rays*, was discovered somewhat later and found to be similar to a lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

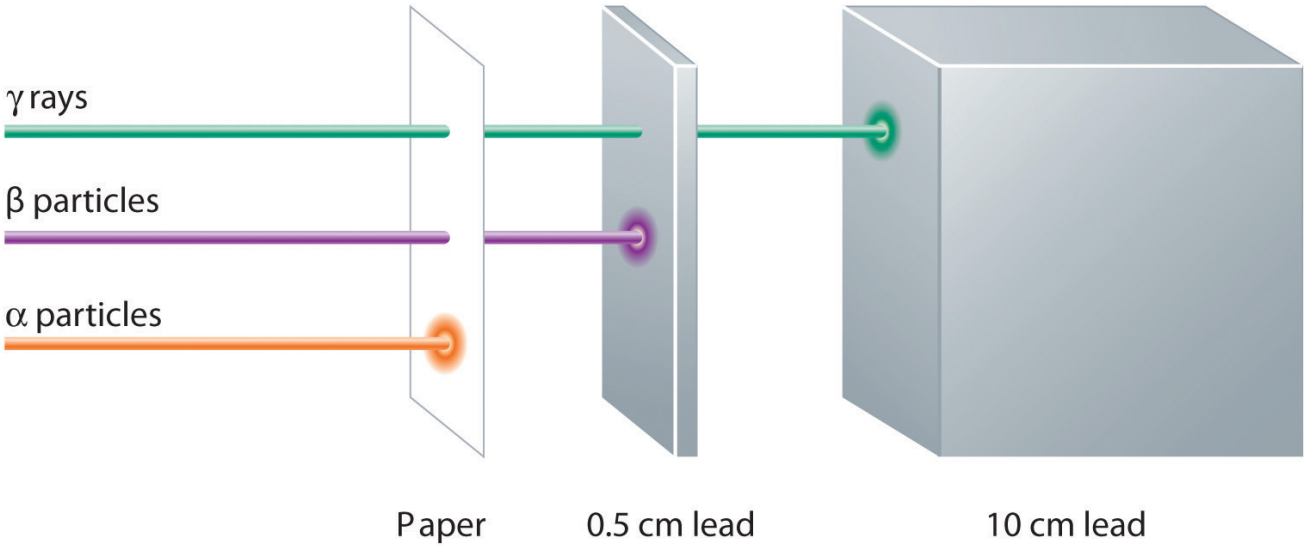
These three kinds of radiation—α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As Figure 1.6.3" illustrates, α particles and β particles are deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields. Figure 1.6.4 shows that α particles have the least penetrating power and are stopped by a sheet of paper, whereas β particles can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, γ-rays can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

Figure 1.6.3 *Effect of an Electric Field on α Particles, β Particles, and γ Rays*




*A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.)*

Figure 1.6.4 *Relative Penetrating Power of the Three Types of Radiation*

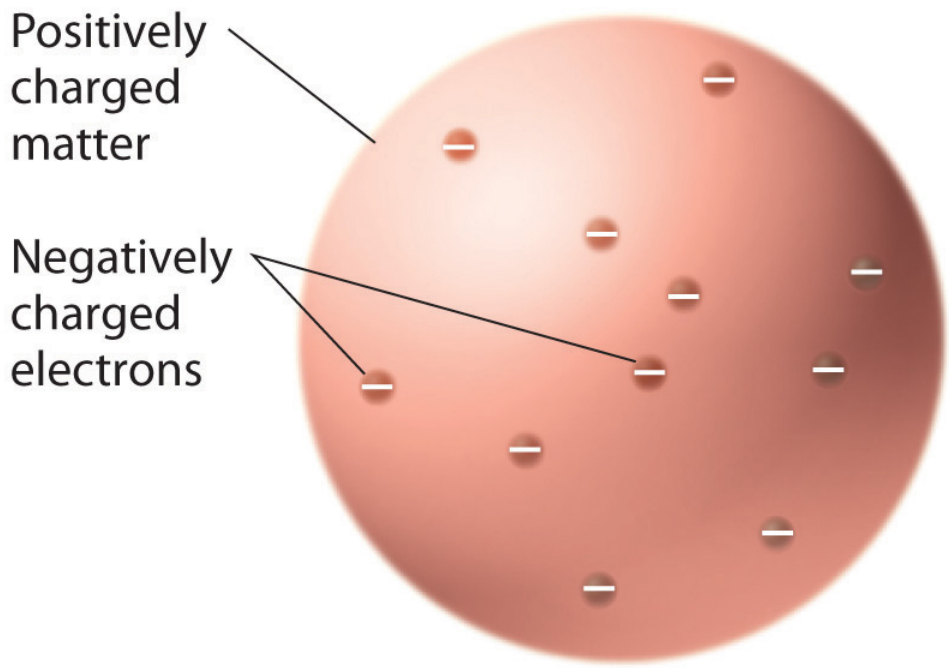



*A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them.*

## The Atomic Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 1.6.5").

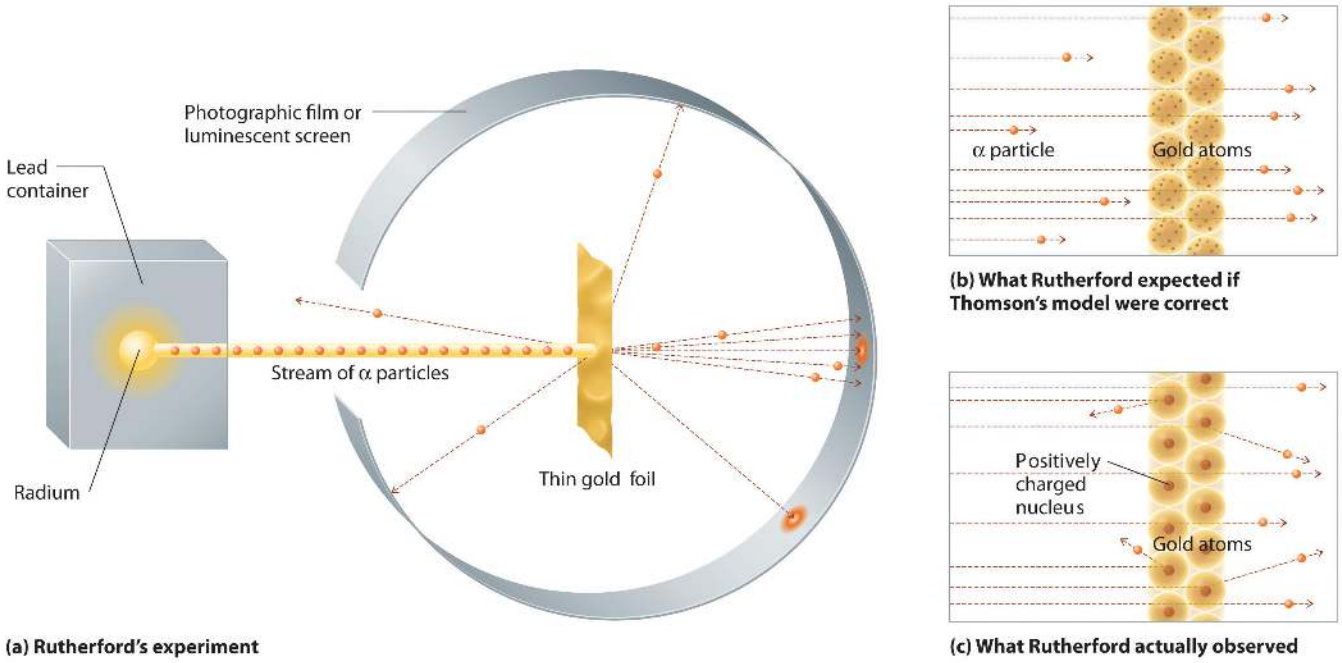
Figure 1.6.5 *Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom*




*In this model, the electrons are embedded in a uniform sphere of positive charge.*

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was impossible. Rutherford aimed a stream of α particles at a very thin gold foil target (part (a) in Figure 1.6.6) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets with a thickness that minimized the number of atoms in the target. If Thomson's model of the atom were correct, the positively charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (part (b) in Figure 1.6.6). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (part (c) inFigure 1.6.6). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

Figure 1.6.6 *A Summary of Rutherford's Experiments*




*(a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) But a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus.*

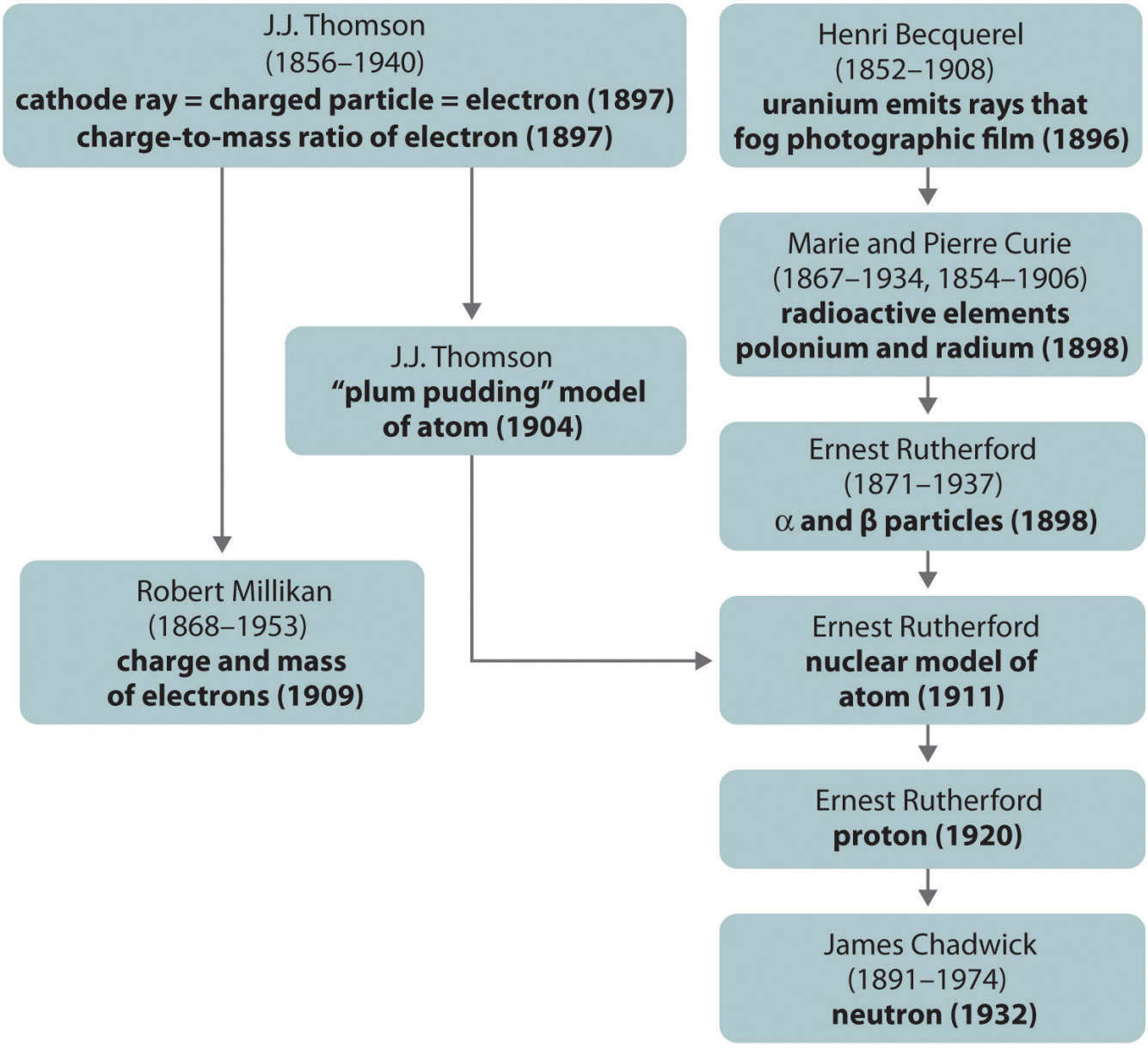
Rutherford's results were *not* consistent with a model in which the mass and positive charge are distributed uniformly throughout the volume of an atom. Instead, they strongly suggested that both the mass and positive charge are concentrated in a tiny fraction of the volume of an atom, which Rutherford called the **nucleus**. It made sense that a small fraction of the α particles collided with the dense, positively charged nuclei in either a glancing fashion, resulting in large deflections, or almost head-on, causing them to be reflected straight back at the source.

Although Rutherford could not explain why repulsions between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsions between negatively charged electrons would cause the electrons to be uniformly distributed throughout the atom's volume.Today we know that *strong nuclear forces*, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus. For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he thought that physics was superior to chemistry. In his opinion, "All science is either physics or stamp collecting." (The authors of this text do *not* share Rutherford's view!)

Subsequently, Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name *proton* in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons and is therefore simply the nucleus of a helium atom.

The historical development of the different models of the atom's structure is summarized in Figure 1.6.7. Rutherford's model of the atom is essentially the same as the modern one, except that we now know that electrons are *not* uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described in Chapter 6. Figure 1.6.8 shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

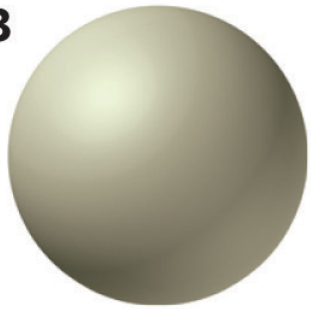
Figure 1.6.8 *A Summary of the Historical Development of Models of the Components and Structure of the Atom*




*The dates in parentheses are the years in which the key experiments were performed.*

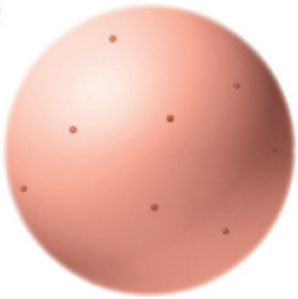
Figure 1.6.9 *The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom*

**1803**



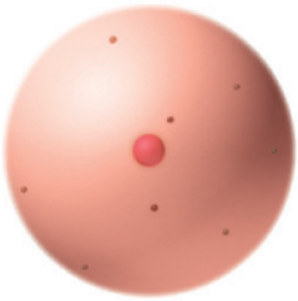
Dalton proposes the indivisible unit of an element is the atom.

**1904**



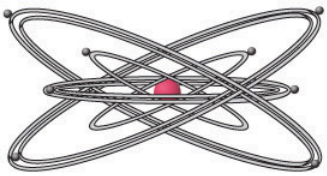
Thomson discovers electrons, believed to reside within a sphere of uniform positive charge (the plum pudding model).

**1911**



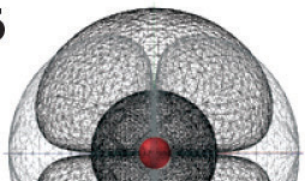
Rutherford demonstrates the existence of a positively charged nucleus that contains nearly all the mass of an atom.

**1913**

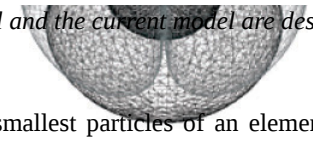


Bohr proposes fixed circular orbits around the nucleus for electrons.

**1926**



In the current model of the atom, electrons occupy regions of




*Bohr's model and the current model are described in Chapter 6.*

## Summary

Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged **electrons** around a central **nucleus** composed of more massive positively charged **protons** and electrically neutral **neutrons**. **Radioactivity** is the emission of energetic particles and rays (radiation) by some substances. Three important kinds of radiation are α particles (helium nuclei), β particles (electrons traveling at high speed), and γ rays (similar to x-rays but higher in energy).

## KEY TAKEAWAY

- The atom consists of discrete particles that govern its chemical and physical behavior.

## CONCEPTUAL PROBLEMS

1. Describe the experiment that provided evidence that the proton is positively charged.
2. What observation led Rutherford to propose the existence of the neutron?
3. What is the difference between Rutherford's model of the atom and the model chemists use today?
4. If cathode rays are not deflected when they pass through a region of space, what does this imply about the presence or absence of a magnetic field perpendicular to the path of the rays in that region?
5. Describe the outcome that would be expected from Rutherford's experiment if the charge on α particles had remained the same but the nucleus were negatively charged. If the nucleus were neutral, what would have been the outcome?
6. Describe the differences between an α particle, a β particle, and a γ ray. Which has the greatest ability to penetrate matter?

## NUMERICAL PROBLEMS

*Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9) before proceeding to the Numerical Problems.*

1. Using the data in Table 1.6.1 and the periodic table (see Periodic Table of Elements"), calculate the percentage of the mass of a silicon atom that is due to
    1. electrons.
    2. protons.
2. Using the data in Table 1.6.1 and the periodic table (see Periodic Table of Elements"), calculate the percentage of the mass of a helium atom that is due to
    1. electrons.
    2. protons.
3. The radius of an atom is approximately $10^4$ times larger than the radius of its nucleus. If the radius of the nucleus were 1.0 cm, what would be the radius of the atom in centimeters? in miles?
4. The total charge on an oil drop was found to be $3.84 \times 10^{-18}$ coulombs. What is the total number of electrons contained in the drop?

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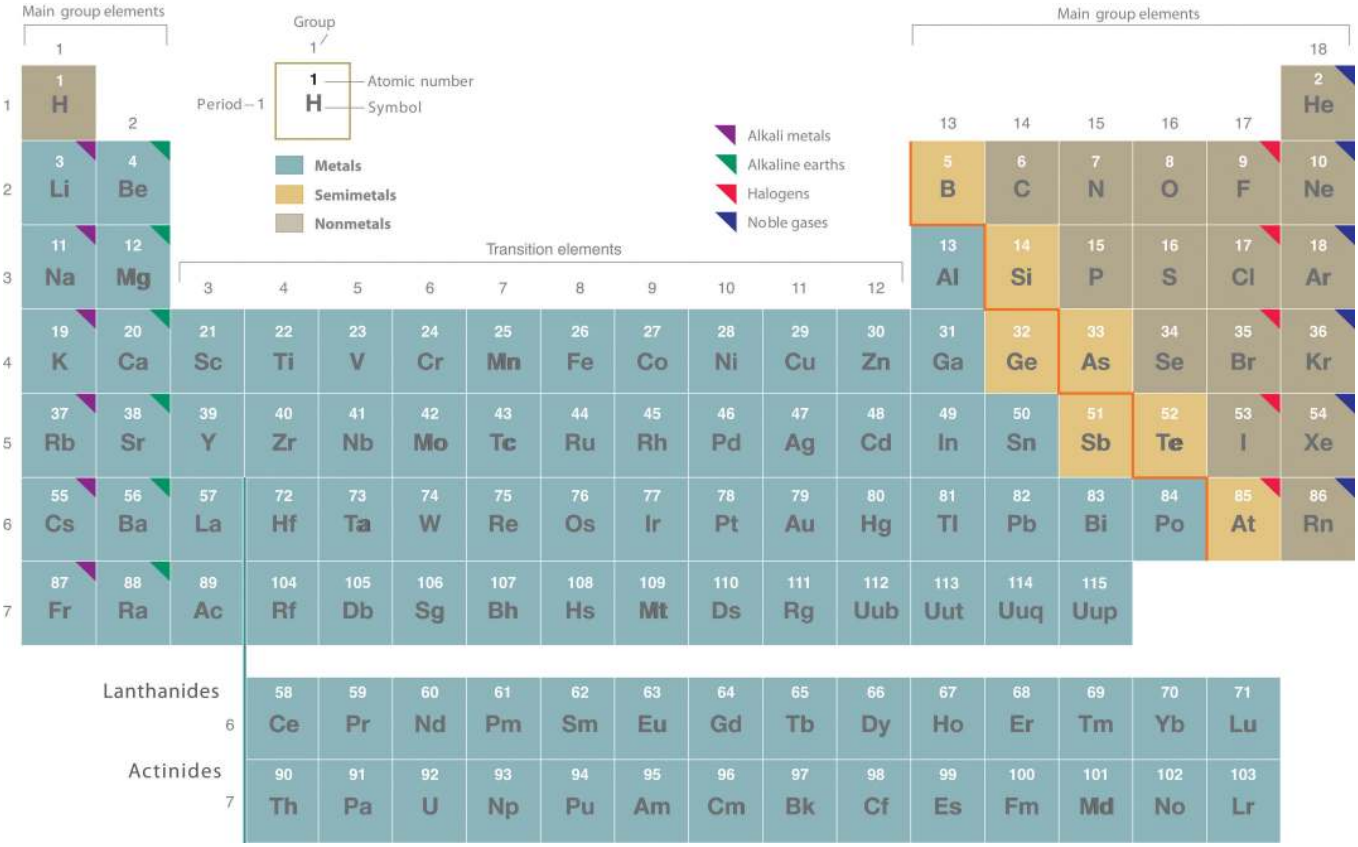
# 1.7: Isotopes and Atomic Masses

**Learning Objectives**

- To know the meaning of isotopes and atomic masses.

Rutherford's nuclear model of the atom helped explain why atoms of different elements exhibit different chemical behavior. The identity of an element is defined by its **atomic number (*Z*)**, the number of protons in the nucleus of an atom of the element. *The atomic number is therefore different for each element*. The known elements are arranged in order of increasing *Z* in the **periodic table** ( Figure 1.7.1 ),We will explain the rationale for the peculiar format of the periodic table in Chapter 7. in which each element is assigned a unique one-, two-, or three-letter symbol. The names of the elements are listed in the periodic table, along with their symbols, atomic numbers, and atomic masses. The chemistry of each element is determined by its number of protons and electrons. In a neutral atom, the number of electrons equals the number of protons.

Figure 1.7.1 *The Periodic Table Showing the Elements in Order of Increasing Z*




*As described in Section 1.8, the metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals.*

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to remind us of their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table 1.7.1. As you work through

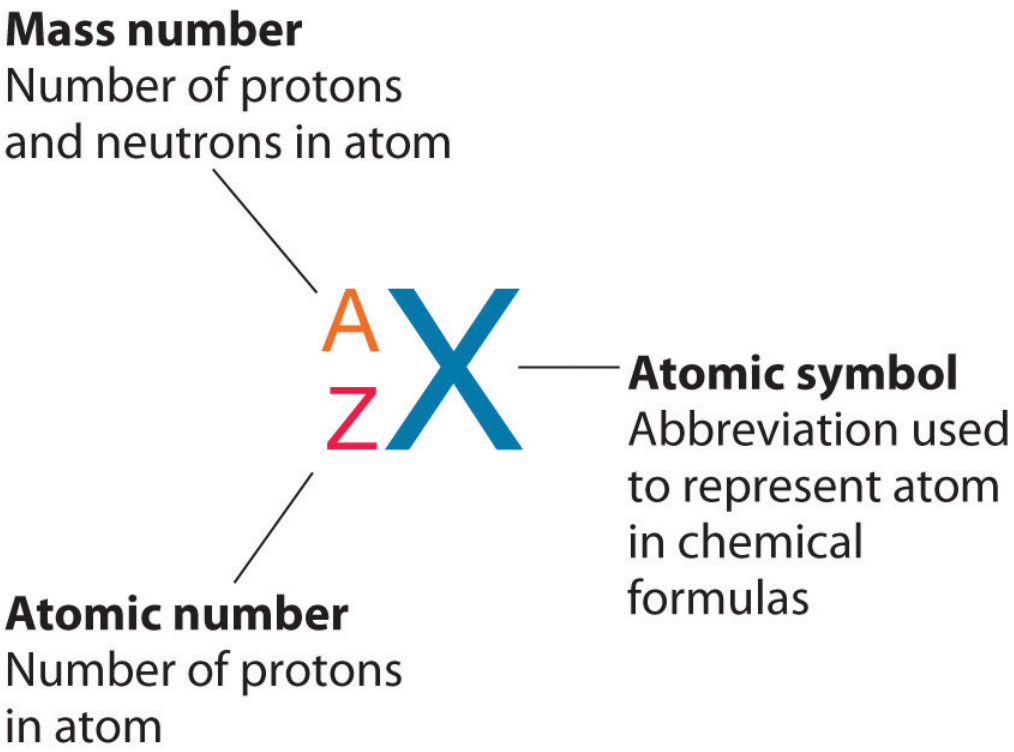
this text, you will encounter the names and symbols of the elements repeatedly, and much as you become familiar with characters in a play or a film, their names and symbols will become familiar.

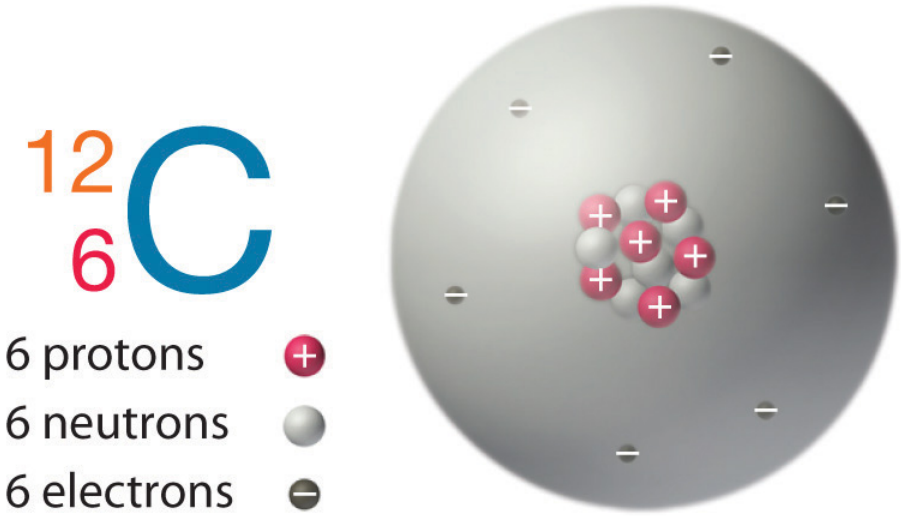
Table 1.7.1 Element Symbols Based on Names No Longer in Use

| Element | Symbol | Derivation | Meaning |
|---|---|---|---|
| antimony | Sb | *stibium* | Latin for “mark” |
| copper | Cu | *cuprum* | from *Cyprium*, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire |
| gold | Au | *aurum* | Latin for “gold” |
| iron | Fe | *ferrum* | Latin for “iron” |
| lead | Pb | *plumbum* | Latin for “heavy” |
| mercury | Hg | *hydrargyrum* | Latin for “liquid silver” |
| potassium | K | *kalium* | from the Arabic *al-qili*, “alkali” |
| silver | Ag | *argentum* | Latin for “silver” |
| sodium | Na | *natrium* | Latin for “sodium” |
| tin | Sn | *stannum* | Latin for “tin” |
| tungsten | W | *wolfram* | German for “wolf stone” because it interfered with the smelting of tin and was thought to devour the tin |

Recall from Section 1.6 that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have *the same number of protons*, and hence the same atomic number, but *different numbers of neutrons* are called **isotopes**. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the **mass number (*A*)**, the sum of the numbers of protons and neutrons.

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as XZA, where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore C612. The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies *Z*. Consequently, C612 is more often written as $^{12}$C, which is read as “carbon-12.” Nevertheless, the value of *Z* is commonly included in the notation for *nuclear* reactions because these reactions involve changes in *Z*, as described in Chapter 20.




In addition to $^{12}C$, a typical sample of carbon contains 1.11% C613 ($^{13}C$), with 7 neutrons and 6 protons, and a trace of C614 ($^{14}C$), with 8 neutrons and 6 protons. The nucleus of $^{14}C$ is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology (see Chapter 14). Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table 1.7.2.

Table 1.7.2 Properties of Selected Isotopes

| Element | Symbol | Atomic Mass (amu) | Isotope Mass Number | Isotope Masses (amu) | Percent Abundances (%) |
|---|---|---|---|---|---|
| hydrogen | H | 1.0079 | 1 | 1.007825 | 99.9855 |
| | | | 2 | 2.014102 | 0.0115 |
| boron | B | 10.81 | 10 | 10.012937 | 19.91 |
| | | | 11 | 11.009305 | 80.09 |
| carbon | C | 12.011 | 12 | 12 (defined) | 99.89 |
| | | | 13 | 13.003355 | 1.11 |
| oxygen | O | 15.9994 | 16 | 15.994915 | 99.757 |
| | | | 17 | 16.999132 | 0.0378 |
| | | | 18 | 17.999161 | 0.205 |
| iron | Fe | 55.845 | 54 | 53.939611 | 5.82 |
| | | | 56 | 55.934938 | 91.66 |
| | | | 57 | 56.935394 | 2.19 |
| | | | 58 | 57.933276 | 0.33 |
| uranium | U | 238.03 | 234 | 234.040952 | 0.0054 |
| | | | 235 | 235.043930 | 0.7204 |
| | | | 238 | 238.050788 | 99.274 |

Sources of isotope data: G. Audi et al., *Nuclear Physics A* 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, *Chemistry and Chemical Reactivity*, 2nd ed., 1991.

### Example 1.7.1

**Given:** number of protons and neutrons

**Asked for:** element and atomic symbol

**Strategy:**

**A** Refer to the periodic table (see Chapter 32) and use the number of protons to identify the element.

**B** Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.

**C** Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

**Solution**

**A** The element with 82 protons (atomic number of 82) is lead: Pb.

**B** For the first isotope, $A$ = 82 protons + 124 neutrons = 206. Similarly, $A$ = 82 + 125 = 207 and $A$ = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are P82206b,P82207b, and P82208b, which are usually abbreviated as $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb.

**? Exercise 1.7.1**

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

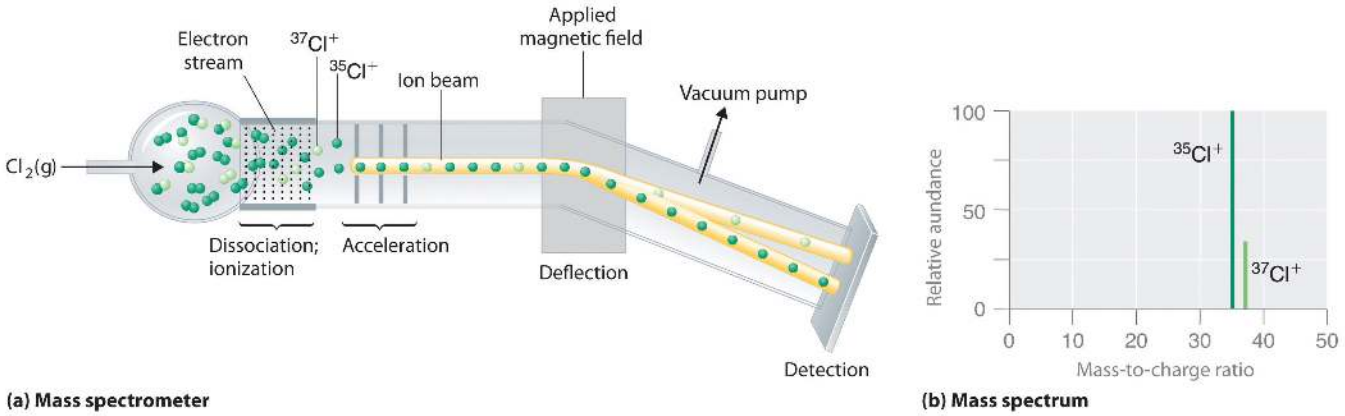
**Answer**

**Answer:** $_{35}{}^{79}B$ and $_{3581}B$ or, more commonly, $^{79}Br$ and $^{81}Br$.

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision (Table 1.3), the mass of any given atom is not simply the sum of the masses of its electrons, protons, and neutrons. For example, the ratio of the masses of $^{1}H$ (hydrogen) and $^{2}H$ (deuterium) is actually 0.500384, rather than 0.49979 as predicted from the numbers of neutrons and protons present. Although the difference in mass is small, it is extremely important because it is the source of the huge amounts of energy released in nuclear reactions (Chapter 20).

Because atoms are much too small to measure individually and do not have a charge, there is no convenient way to accurately measure *absolute* atomic masses. Scientists can measure *relative* atomic masses very accurately, however, using an instrument called a *mass spectrometer*. The technique is conceptually similar to the one Thomson used to determine the mass-to-charge ratio of the electron. First, electrons are removed from or added to atoms or molecules, thus producing charged particles called **ions**. When an electric field is applied, the ions are accelerated into a separate chamber where they are deflected from their initial trajectory by a magnetic field, like the electrons in Thomson's experiment. The extent of the deflection depends on the mass-to-charge ratio of the ion. By measuring the relative deflection of ions that have the same charge, scientists can determine their relative masses (Figure 1.25). Thus it is not possible to calculate absolute atomic masses accurately by simply adding together the masses of the electrons, the protons, and the neutrons, and *absolute* atomic masses cannot be measured, but *relative* masses can be measured very accurately. It is actually rather common in chemistry to encounter a quantity whose magnitude can be measured only relative to some other quantity, rather than absolutely. We will encounter many other examples later in this text. In such cases, chemists usually define a standard by arbitrarily assigning a numerical value to one of the quantities, which allows them to calculate numerical values for the rest.

Figure 1.25 Determining Relative Atomic Masses Using a Mass Spectrometer




*Chlorine consists of two isotopes, $^{35}Cl$ and $^{37}Cl$, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the $Cl_2$ molecules into chlorine atoms and convert the chlorine atoms to $Cl^+$ ions. The ions are then accelerated into a magnetic field. The extent to which the ions are deflected by the magnetic field depends on their relative mass-to-charge ratios. Note that the lighter $^{35}Cl^+$ ions are deflected more than the heavier $^{37}Cl^+$ ions. By measuring the relative deflections of the ions, chemists can determine their mass-to-charge ratios and thus their masses. (b) Each peak in the mass spectrum corresponds to an ion with a particular mass-to-charge ratio. The abundance of the two isotopes can be determined from the heights of the peaks.*

The arbitrary standard that has been established for describing atomic mass is the **atomic mass unit (amu)**, defined as one-twelfth of the mass of one atom of $^{12}C$. Because the masses of all other atoms are calculated relative to the $^{12}C$ standard, $^{12}C$ is the only atom listed in Table 1.7.2 " whose exact atomic mass is equal to the mass number. Experiments have shown that 1 amu = $1.66 \times 10^{-24}$ g.

Mass spectrometric experiments give a value of 0.167842 for the ratio of the mass of $^{2}H$ to the mass of $^{12}C$, so the absolute mass of $^{2}H$ is

mass of H2mass of C12×mass of C12= 0.167842 × 12 amu = 2.104104 amu

The masses of the other elements are determined in a similar way.

The periodic table lists the atomic masses of all the elements. If you compare these values with those given for some of the isotopes in Table 1.7.2 , you can see that the atomic masses given in the periodic table never correspond exactly to those of any of the isotopes. Because most elements exist as mixtures of several stable isotopes, the **atomic mass** of an element is defined as the weighted average of the masses of the isotopes. For example, naturally occurring carbon is largely a mixture of two isotopes: 98.89% $^{12}C$ (mass = 12 amu by definition) and 1.11% $^{13}C$ (mass = 13.003355 amu). The percent abundance of $^{14}C$ is so low that it can be ignored in this calculation. The *average* atomic mass of carbon is then calculated as

$$(0.9889 \times 12amu) + (0.0111 \times 13.003355amu) = 12.01amu$$

Carbon is predominantly $^{12}C$, so its average atomic mass should be close to 12 amu, which is in agreement with our calculation.

The value of 12.01 is shown under the symbol for C in the periodic table , although without the abbreviation *amu*, which is customarily omitted. Thus the tabulated *atomic mass* of carbon or any other element is the weighted average of the masses of the naturally occurring isotopes.

### Example 1.7.1

Naturally occurring bromine consists of the two isotopes listed in the following table:

| Isotope | Exact Mass (amu) | Percent Abundance (%) |
|---|---|---|
| $^{79}Br$ | 78.9183 | 50.69 |
| $^{81}Br$ | 80.9163 | 49.31 |

Calculate the atomic mass of bromine.

**Given:** exact mass and percent abundance

**Asked for:** atomic mass

**Strategy:**

**A** Convert the percent abundances to decimal form to obtain the mass fraction of each isotope.

**B** Multiply the exact mass of each isotope by its corresponding mass fraction (percent abundance ÷ 100) to obtain its weighted mass.

**C** Add together the weighted masses to obtain the atomic mass of the element.

**D** Check to make sure that your answer makes sense.

**Solution**

**A** The atomic mass is the weighted average of the masses of the isotopes. In general, we can write

atomic mass of element = [(mass of isotope 1 in amu) (mass fraction of isotope 1)] + [(mass of isotope 2) (mass fraction of isotope 2)] + …

Bromine has only two isotopes. Converting the percent abundances to mass fractions gives

B79r: 50.69100=0.5069 B81r: 49.31100=0.4931

**B** Multiplying the exact mass of each isotope by the corresponding mass fraction gives the isotope's weighted mass:

$^{79}Br$: 79.9183 amu × 0.5069 = 40.00 amu$^{81}Br$: 80.9163 amu × 0.4931 = 39.90 amu

**C** The sum of the weighted masses is the atomic mass of bromine is

40.00 amu + 39.90 amu = 79.90 amu

**D** This value is about halfway between the masses of the two isotopes, which is expected because the percent abundance of each is approximately 50%.

**? Exercise 1.7.1**

Magnesium has the three isotopes listed in the following table:

| Isotope | Exact Mass (amu) | Percent Abundance (%) |
|---|---|---|
| $^{24}$Mg | 23.98504 | 78.70 |
| $^{25}$Mg | 24.98584 | 10.13 |
| $^{26}$Mg | 25.98259 | 11.17 |

Use these data to calculate the atomic mass of magnesium.

**Answer**

24.31 amu

## Summary

Each atom of an element contains the same number of protons, which is the **atomic number** (*Z*). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (*A*), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit** (**amu**), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons. The **atomic mass** of an element is the weighted average of the masses of the naturally occurring isotopes. When one or more electrons are added to or removed from an atom or molecule, a charged particle called an **ion** is produced, whose charge is indicated by a superscript after the symbol.

## KEY TAKEAWAY

- The mass of an atom is a weighted average that is largely determined by the number of its protons and neutrons, whereas the number of protons and electrons determines its charge.

## CONCEPTUAL PROBLEMS

1. Complete the following table for the missing elements, symbols, and numbers of electrons.

| Element | Symbol | Number of Electrons |
|---|---|---|
| molybdenum | | |
| | | 19 |
| titanium | | |
| | B | |
| | | 53 |
| | Sm | |
| helium | | |
| | | 14 |

2. Complete the following table for the missing elements, symbols, and numbers of electrons.

| Element | Symbol | Number of Electrons |
|---|---|---|
| lanthanum | | |
| | Ir | |
| aluminum | | |
| | | 80 |
| sodium | | |
| | Si | |
| | | 9 |
| | Be | |

3. Is the mass of an ion the same as the mass of its parent atom? Explain your answer.
4. What isotopic standard is used for determining the mass of an atom?
5. Give the symbol XZA for these elements, all of which exist as a single isotope.
    1. beryllium
    2. ruthenium
    3. phosphorus
    4. aluminum
    5. cesium
    6. praseodymium
    7. cobalt
    8. yttrium
    9. arsenic
6. Give the symbol XZA for these elements, all of which exist as a single isotope.
    1. fluorine
    2. helium
    3. terbium
    4. iodine
    5. gold
    6. scandium
    7. sodium
    8. niobium
    9. manganese
7. Identify each element, represented by X, that have the given symbols.
    1. X2655
    2. X3374
    3. X1224
    4. X53127
    5. X1840
    6. X63152

## NUMERICAL PROBLEMS

*Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9) before proceeding to the Numerical Problems.*

1. The isotopes $^{131}I$ and $^{60}Co$ are commonly used in medicine. Determine the number of neutrons, protons, and electrons in a neutral atom of each.

2. Determine the number of protons, neutrons, and electrons in a neutral atom of each isotope:
    1. $^{97}Tc$
    2. $^{113}In$
    3. $^{63}Ni$
    4. $^{55}Fe$
3. Both technetium-97 and americium-240 are produced in nuclear reactors. Determine the number of protons, neutrons, and electrons in the neutral atoms of each.
4. The following isotopes are important in archaeological research. How many protons, neutrons, and electrons does a neutral atom of each contain?
    1. $^{207}Pb$
    2. $^{16}O$
    3. $^{40}K$
    4. $^{137}Cs$
    5. $^{40}Ar$
5. Copper, an excellent conductor of heat, has two isotopes: $^{63}Cu$ and $^{65}Cu$. Use the following information to calculate the average atomic mass of copper:

| Isotope | Percent Abundance (%) | Atomic Mass (amu) |
|---|---|---|
| $^{63}Cu$ | 69.09 | 62.9298 |
| $^{65}Cu$ | 30.92 | 64.9278 |

6. Silicon consists of three isotopes with the following percent abundances:

| Isotope | Percent Abundance (%) | Atomic Mass (amu) |
|---|---|---|
| $^{28}Si$ | 92.18 | 27.976926 |
| $^{29}Si$ | 4.71 | 28.976495 |
| $^{30}Si$ | 3.12 | 29.973770 |

    Calculate the average atomic mass of silicon.
7. Complete the following table for neon. The average atomic mass of neon is 20.1797 amu.

| Isotope | Percent Abundance (%) | Atomic Mass (amu) |
|---|---|---|
| $^{20}Ne$ | 90.92 | 19.99244 |
| $^{21}Ne$ | 0.257 | 20.99395 |
| $^{22}Ne$ | | |

8. Are X2863 and X2962 isotopes of the same element? Explain your answer.
9. Complete the following table:

| Isotope | Number of Protons | Number of Neutrons | Number of Electrons |
|---|---|---|---|
| $^{238}X$ | | | 95 |
| $^{238}U$ | | | |
| | 75 | 112 | |

10. Complete the following table:

| Isotope | Number of Protons | Number of Neutrons | Number of Electrons |
|---|---|---|---|
| $^{57}Fe$ | | | |
| $^{40}X$ | | 20 | |
| $^{36}S$ | | | |

11. Using a mass spectrometer, a scientist determined the percent abundances of the isotopes of sulfur to be 95.27% for $^{32}S$, 0.51% for $^{33}S$, and 4.22% for $^{34}S$. Use the atomic mass of sulfur from the periodic table and the following atomic masses to determine whether these data are accurate, assuming that these are the only isotopes of sulfur: 31.972071 amu for $^{32}S$, 32.971459 amu for $^{33}S$, and 33.967867 amu for $^{34}S$.
12. The percent abundances of two of the three isotopes of oxygen are 99.76% for $^{16}O$, and 0.204% for $^{18}O$. Use the atomic mass of oxygen given in the periodic table and the following data to determine the mass of $^{17}O$: 15.994915 amu for $^{16}O$ and 17.999160 amu for $^{18}O$.
13. Which element has the higher proportion by mass in NaI?
14. Which element has the higher proportion by mass in KBr?

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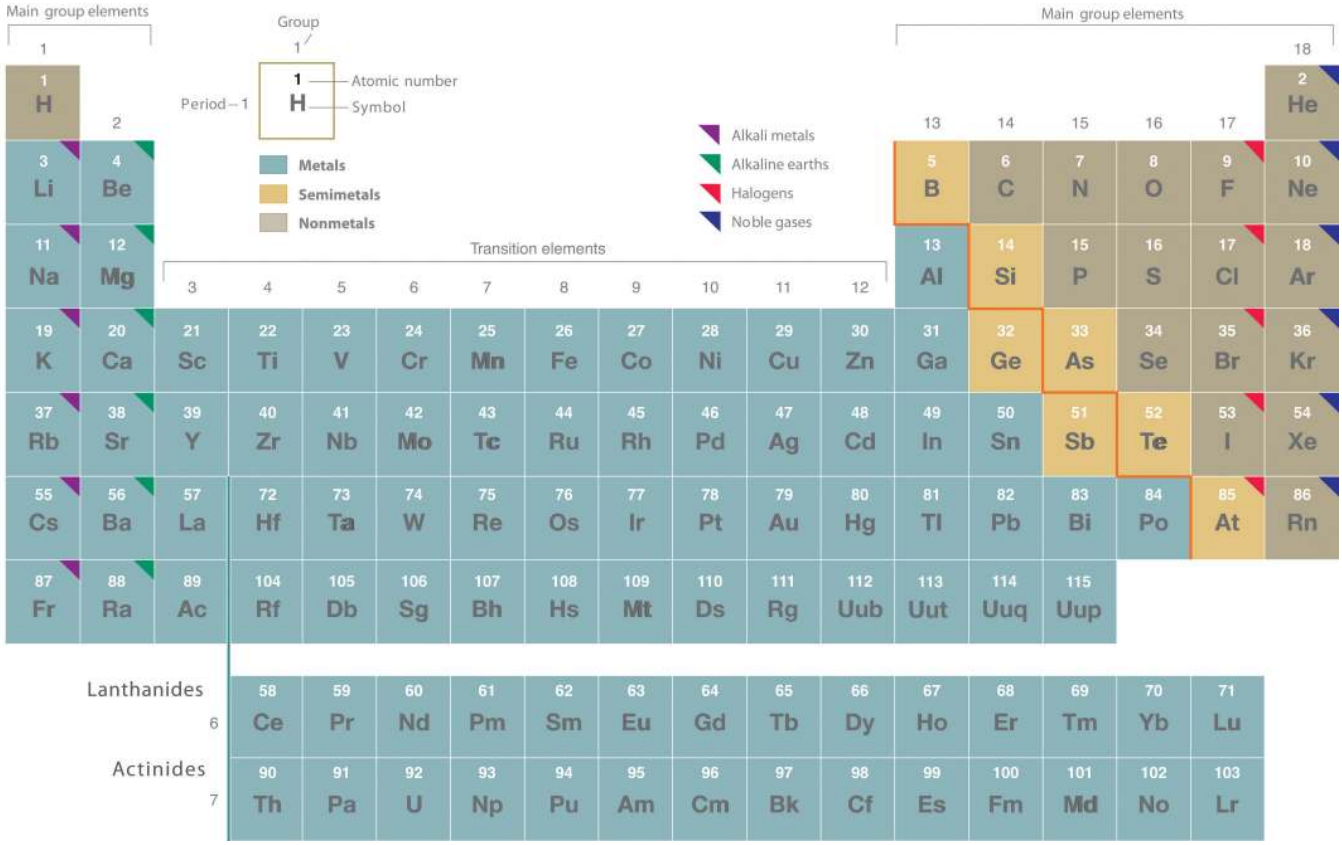
# 1.8: Introduction to the Periodic Table

**Learning Objectives**

- To become familiar with the organization of the periodic table.

The elements are arranged in a **periodic table**, which is probably the single most important learning aid in chemistry. It summarizes huge amounts of information about the elements in a way that permits you to predict many of their properties and chemical reactions. The elements are arranged in seven horizontal rows, in order of increasing atomic number from left to right and top to bottom. The rows are called **periods**, and they are numbered from 1 to 7. The elements are stacked in such a way that elements with similar chemical properties form vertical columns, called **groups**, numbered from 1 to 18 (older periodic tables use a system based on roman numerals). Groups 1, 2, and 13–18 are the **main group elements**, listed as *A* in older tables. Groups 3–12 are in the middle of the periodic table and are the **transition elements**, listed as *B* in older tables. The two rows of 14 elements at the bottom of the periodic table are the *lanthanides* and the *actinides*, whose positions in the periodic table are indicated in group 3. A more comprehensive description of the periodic table is found in Chapter 7.

Figure 1.8.1 *The Periodic Table Showing the Elements in Order of Increasing Z*




*The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals.*

## Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in divides the elements into **metals** (in blue, below and to the left of the line) and **nonmetals** (in bronze, above and to the right of the line). As you might expect, elements colored in gold that lie along the diagonal line exhibit properties intermediate between metals and nonmetals; they are called **semimetals**.

The distinction between metals and nonmetals is one of the most fundamental in chemistry. Metals—such as copper or gold—are good conductors of electricity and heat; they can be pulled into wires because they are **ductile**; they can be hammered or pressed into thin sheets or foils because they are **malleable**; and most have a shiny appearance, so they are **lustrous**. The vast majority of the known elements are metals. Of the metals, only mercury is a liquid at room temperature and pressure; all the rest are solids.

Nonmetals, in contrast, are generally poor conductors of heat and electricity and are not lustrous. Nonmetals can be gases (such as chlorine), liquids (such as bromine), or solids (such as iodine) at room temperature and pressure. Most solid nonmetals are *brittle*, so they break into small pieces when hit with a hammer or pulled into a wire. As expected, semimetals exhibit properties intermediate between metals and nonmetals.

### ✔ Example 1.8.1

**Given:** element

**Asked for:** classification

**Strategy:**

Find selenium in the periodic table and then classify the element according to its location.

**Solution**

The atomic number of selenium is 34, which places it in period 4 and group 16. In selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

### ? Exercise 1.8.1

Based on its location in the periodic table, do you expect indium to be a nonmetal, a metal, or a semimetal?

**Answer**

metal

## Descriptive Names

As we noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of group 1 are known as the **alkali metals**, group 2 are the **alkaline earth metals**, group 17 are the **halogens**, and group 18 are the **noble gases**.

## The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in group 1, but it is not a metal.

The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

## The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rather rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

## The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name *halogen* is derived from the Greek for “salt forming,” which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth’s ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

## The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are **monatomic**. At room temperature and pressure, they are unreactive gases. Because of their lack of reactivity, for many years they were called inert gases or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (*inert*) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

### Note the Pattern

The noble gases are unreactive at room temperature and pressure.

### Summary

The periodic table is an arrangement of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called **groups** (numbered 1–18 from left to right); the seven horizontal rows are called **periods**. Some of the groups have widely used common names, including the **alkali metals** (group 1) and the **alkaline earth metals** (group 2) on the far left, and the **halogens** (group 17) and the **noble gases** (group 18) on the far right. The elements can be broadly divided into **metals**, **nonmetals**, and **semimetals**. Semimetals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semimetals. Metals are **lustrous**, good conductors of electricity, and readily shaped (they are **ductile** and **malleable**), whereas solid nonmetals are generally brittle and poor electrical conductors. Other important groupings of elements in the periodic table are the **main group elements**, the **transition metals**, the lanthanides, and the actinides.

### KEY TAKEAWAY

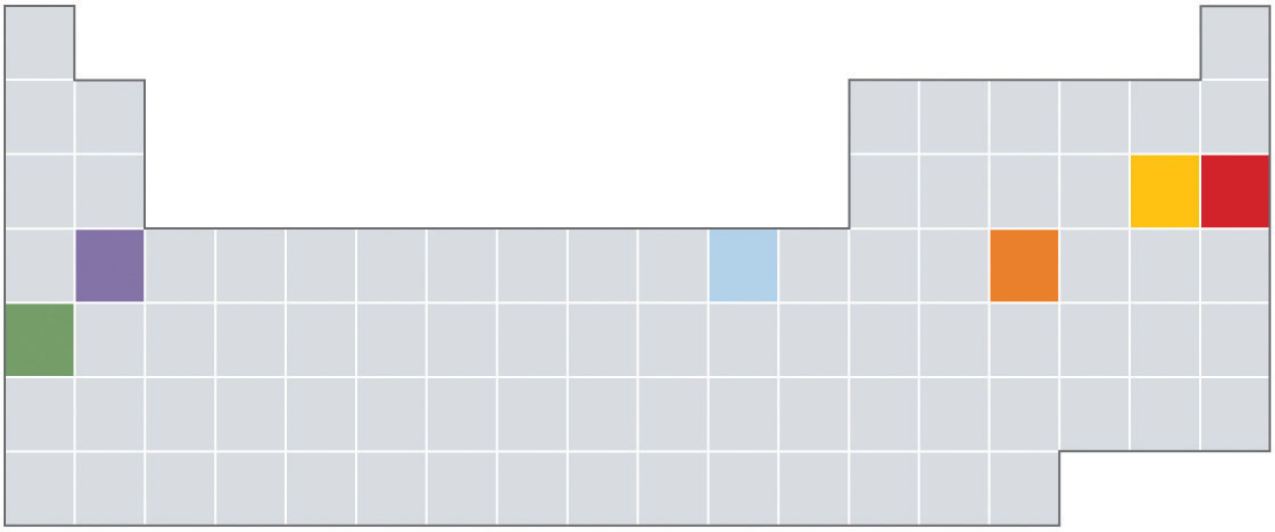
- The periodic table is used as a predictive tool.

### CONCEPTUAL PROBLEMS

1. Classify each element in Conceptual Problem 1 (Section 1.7) as a metal, a nonmetal, or a semimetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.
2. Classify each element in Conceptual Problem 2 (Section 1.7) as a metal, a nonmetal, or a semimetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.
3. Classify each element as a metal, a semimetal, or a nonmetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.
    1. iron
    2. tantalum
    3. sulfur
    4. silicon
    5. chlorine
    6. nickel
    7. potassium
    8. radon

9. zirconium

4. Which of these sets of elements are all in the same period?
    1. potassium, vanadium, and ruthenium
    2. lithium, carbon, and chlorine
    3. sodium, magnesium, and sulfur
    4. chromium, nickel, and krypton
5. Which of these sets of elements are all in the same period?
    1. barium, tungsten, and argon
    2. yttrium, zirconium, and selenium
    3. potassium, calcium, and zinc
    4. scandium, bromine, and manganese
6. Which of these sets of elements are all in the same group?
    1. sodium, rubidium, and barium
    2. nitrogen, phosphorus, and bismuth
    3. copper, silver, and gold
    4. magnesium, strontium, and samarium
7. Which of these sets of elements are all in the same group?
    1. iron, ruthenium, and osmium
    2. nickel, palladium, and lead
    3. iodine, fluorine, and oxygen
    4. boron, aluminum, and gallium
8. Indicate whether each element is a transition metal, a halogen, or a noble gas.
    1. manganese
    2. iridium
    3. fluorine
    4. xenon
    5. lithium
    6. carbon
    7. zinc
    8. sodium
    9. tantalum
    10. hafnium
    11. antimony
    12. cadmium
9. Which of the elements indicated in color in the periodic table shown below is most likely to exist as a monoatomic gas? As a diatomic gas? Which is most likely to be a semimetal? A reactive metal?



10. Based on their locations in the periodic table, would you expect these elements to be malleable? Why or why not?
    1. phosphorus
    2. chromium
    3. rubidium
    4. copper
    5. aluminum
    6. bismuth
    7. neodymium
11. Based on their locations in the periodic table, would you expect these elements to be lustrous? Why or why not?
    1. sulfur
    2. vanadium
    3. nickel
    4. arsenic
    5. strontium
    6. cerium
    7. sodium

## Answer

1.
2.

3.

| Symbol | Type |
|---|---|
| Fe | metal: transition metal |
| Ta | metal: transition metal |
| S | nonmetal |
| Si | semimetal |
| Cl | nonmetal (halogen) |
| Ni | metal: transition metal |
| K | metal: alkali metal |
| Rn | nonmetal (noble gas) |
| Zr | metal: transition metal |

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# 1.9: Essential Elements for Life

**Learning Objective**

- To understand the importance of elements to nutrition.

Of the approximately 115 elements known, only the 19 highlighted in purple in Figure 1.9.1 are absolutely required in the human diet. These elements—called essential elements—are restricted to the first four rows of the periodic table, with only two or three exceptions (molybdenum, iodine, and possibly tin in the fifth row). Some other elements are essential for specific organisms. For example, boron is required for the growth of certain plants, bromine is widely distributed in marine organisms, and tungsten is necessary for some microorganisms.

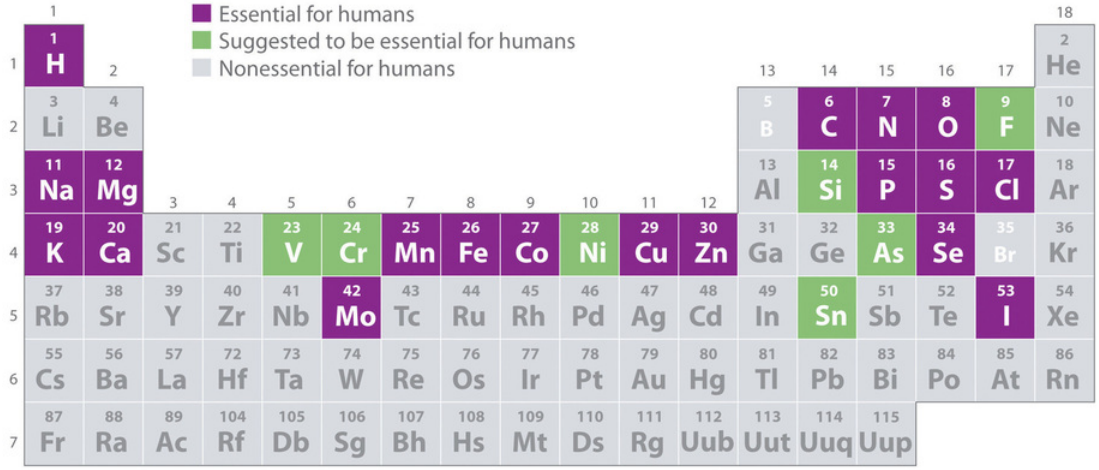



Figure 1.9.1: The Essential Elements in the Periodic Table. Elements that are known to be essential for human life are shown in purple; elements that are suggested to be essential are shown in green. Elements not known to be essential are shown in gray.

What makes an element “essential”? By definition, an essential element is one that is required for life and whose absence results in death. Because of the experimental difficulties involved in producing deficiencies severe enough to cause death, especially for elements that are required in very low concentrations in the diet, a somewhat broader definition is generally used. An element is considered to be essential if a deficiency consistently causes abnormal development or functioning and if dietary supplementation of that element—and only that element—prevents this adverse effect. Scientists determine whether an element is essential by raising rats, chicks, and other animals on a synthetic diet that has been carefully analyzed and supplemented with acceptable levels of all elements except the element of interest (E). Ultraclean environments, in which plastic cages are used and dust from the air is carefully removed, minimize inadvertent contamination. If the animals grow normally on a diet that is as low as possible in E, then either E is not an essential element or the diet is not yet below the minimum required concentration. If the animals do not grow normally on a low-E diet, then their diets are supplemented with E until a level is reached at which the animals grow normally. This level is the minimum required intake of element E.

## Classification of the Essential Elements

The approximate elemental composition of a healthy 70.0 kg (154 lb) adult human is listed in Table 1.9.1. Note that most living matter consists primarily of the so-called bulk elements: oxygen, carbon, hydrogen, nitrogen, and sulfur—the building blocks of the compounds that constitute our organs and muscles. These five elements also constitute the bulk of our diet; tens of grams per day are required for humans. Six other elements—sodium, magnesium, potassium, calcium, chlorine, and phosphorus—are often referred to as macrominerals because they provide essential ions in body fluids and form the major structural components of the body. In addition, phosphorus is a key constituent of both DNA and RNA: the genetic building blocks of living organisms. The six macrominerals are present in the body in somewhat smaller amounts than the bulk elements, so correspondingly lower levels are required in the diet. The remaining essential elements—called trace elements—are present in very small amounts, ranging from a few grams to a few milligrams in an adult human. Finally, measurable levels of some elements are found in humans but are not required for growth or good health. Examples are rubidium and strontium, whose chemistry is similar to that of the elements

immediately above them in the periodic table (potassium and calcium, respectively, which are essential elements). Because the body's mechanisms for extracting potassium and calcium from foods are not 100% selective, small amounts of rubidium and strontium, which have no known biological function, are absorbed.

Table 1.9.1: Approximate Elemental Composition of a Typical 70 kg Human

| Bulk Elements (kg) | | Macrominerals (g) | |
|---|---|---|---|
| oxygen | 44 | calcium | 1700 |
| carbon | 12.6 | phosphorus | 680 |
| hydrogen | 6.6 | potassium | 250 |
| nitrogen | 1.8 | chlorine | 115 |
| sulfur | 0.1 | sodium | 70 |
| | | magnesium | 42 |
| Trace Elements (mg) | | | |
| iron | 5000 | lead | 35 |
| silicon | 3000 | barium | 21 |
| zinc | 1750 | molybdenum | 14 |
| rubidium | 360 | boron | 14 |
| copper | 280 | arsenic | ~3 |
| strontium | 280 | cobalt | ~3 |
| bromine | 140 | chromium | ~3 |
| tin | 140 | nickel | ~3 |
| manganese | 70 | selenium | ~2 |
| iodine | 70 | lithium | ~2 |
| aluminum | 35 | vanadium | ~2 |

## The Trace Elements

Because it is difficult to detect low levels of some essential elements, the trace elements were relatively slow to be recognized as essential. Iron was the first. In the 17th century, anemia was proved to be caused by an iron deficiency and often was cured by supplementing the diet with extracts of rusty nails. It was not until the 19th century, however, that trace amounts of iodine were found to eliminate goiter (an enlarged thyroid gland). This is why common table salt is "iodized": a small amount of iodine is added. Copper was shown to be essential for humans in 1928, and manganese, zinc, and cobalt soon after that. Molybdenum was not known to be an essential element until 1953, and the need for chromium, selenium, vanadium, fluorine, and silicon was demonstrated only in the last 50 years. It seems likely that in the future other elements, possibly including tin, will be found to be essential at very low levels.

Many compounds of trace elements, such as arsenic, selenium, and chromium, are toxic and can even cause cancer, yet these elements are identified as essential elements in Figure 1.9.1. In fact, there is some evidence that one bacterium has replaced phosphorus with arsenic, although the finding is controversial. This has opened up the possibility of a "shadow biosphere" on Earth in which life evolved from an as yet undetected common ancestor. How can elements toxic to life be essential? First, the toxicity of an element often depends on its chemical form—for example, only certain compounds of chromium are toxic, whereas others are used in mineral supplements. Second, as shown in Figure 1.9.2, every element has three possible levels of dietary intake: deficient, optimum, and toxic in order of increasing concentration in the diet. Very low intake levels lead to symptoms of deficiency. Over

some range of higher intake levels, an organism is able to maintain its tissue concentrations of the element at a level that optimizes biological functions. Finally, at some higher intake level, the normal regulatory mechanisms are overloaded, causing toxic symptoms to appear. Each element has its own characteristic curve. Both the width of the plateau and the specific concentration corresponding to the center of the plateau region differ by as much as several orders of magnitude for different elements. In the adult human, for example, the recommended daily dietary intake is 10–18 mg of iron, 2–3 mg of copper, and less than 0.1 mg of chromium and selenium.

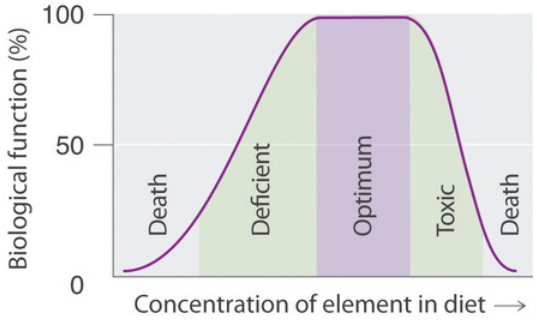



Figure 1.9.2: Possible Concentrations of an Essential Element in the Diet. The deficient, optimum, and toxic concentrations are different for different elements.

## Amplification

How can elements that are present in such minuscule amounts have such large effects on an organism's health? Our knowledge of the pathways by which each of the known trace elements affects health is far from complete, but certain general features are clear. The trace elements participate in an amplification mechanism; that is, they are essential components of larger biological molecules that are capable of interacting with or regulating the levels of relatively large amounts of other molecules. For example, vitamin $B_{12}$ contains a single atom of cobalt, which is essential for its biological function. If the molecule whose level is controlled by the trace element can regulate the level of another molecule, and more and more molecules, then the potential exists for extreme amplification of small variations in the level of the trace element. One goal of modern chemical research is to elucidate in detail the roles of the essential elements. In subsequent chapters, we will introduce some results of this research to demonstrate the biological importance of many of the elements and their compounds.

## Summary

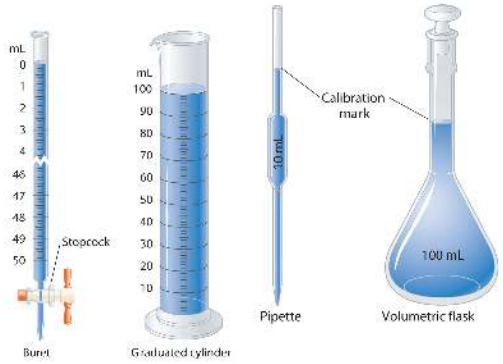
About 19 of the approximately 115 known elements are essential for humans. An essential element is one whose absence results in abnormal biological function or development that is prevented by dietary supplementation with that element. Living organisms contain relatively large amounts of oxygen, carbon, hydrogen, nitrogen, and sulfur (these five elements are known as the bulk elements), along with sodium, magnesium, potassium, calcium, chlorine, and phosphorus (these six elements are known as macrominerals). The other essential elements are the trace elements, which are present in very small quantities. Dietary intakes of elements range from deficient to optimum to toxic with increasing quantities; the optimum levels differ greatly for the essential elements.

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# 1.10: Essential Skills 1

This section describes some of the fundamental mathematical skills you will need to complete the questions and problems in this text. For some of you, this discussion will serve as a review, whereas others may be encountering at least some of the ideas and techniques for the first time.

## Instruments of Measurement




**(left) Graduated glassware** *is used to deliver variable volumes of liquid.* (Right) **Volumetric glassware** *is used to deliver (pipette) or contain (volumetric flask) a single volume accurately when filled to the calibration mark.*




A **balance** is used to measure mass.

A variety of instruments are available for making direct measurements of the macroscopic properties of a chemical substance. For example, we usually measure the volume of a liquid sample with pipettes, burets, graduated cylinders, and volumetric flasks, whereas we usually measure the mass of a solid or liquid substance with a balance. Measurements on an atomic or molecular scale, in contrast, require specialized instrumentation, such as the mass spectrometer described in Section 1.6 "Isotopes and Atomic Masses".

### SI Units

All reported measurements must include an appropriate unit of measurement because to say that a substance has “a mass of 10,” for example, does not tell whether the mass was measured in grams, pounds, tons, or some other unit. To establish worldwide standards for the consistent measurement of important physical and chemical properties, an international body called the General Conference on Weights and Measures devised the Système internationale d’unités (or SI). The International System of Units is based on metric units and requires that measurements be expressed in decimal form. Table 1.7 lists the seven base units of the SI system; all other SI units of measurement are derived from them.

Table 1.7 SI Base Units

| Base Quantity | Unit Name | Abbreviation |
|---|---|---|
| mass | kilogram | kg |
| length | meter | m |
| time | second | s |
| temperature | kelvin | K |
| electric current | ampere | A |
| amount of substance | mole | mol |
| luminous intensity | candela | cd |

By attaching prefixes to the base unit, the magnitude of the unit is indicated; each prefix indicates that the base unit is multiplied by a specified power of 10. The prefixes, their symbols, and their numerical significance are given in Table 1.8. To study chemistry, you need to know the information presented in Table 1.7 and Table 1.8 .

Table 1.8 Prefixes Used with SI Units

| Prefix | Symbol | Value | Power of 10 | Meaning |
|---|---|---|---|---|
| tera | T | 1,000,000,000,000 | 1012 | trillion |
| giga | G | 1,000,000,000 | 109 | billion |
| mega | M | 1,000,000 | 106 | million |
| kilo | k | 1000 | 103 | thousand |
| hecto | h | 100 | 102 | hundred |
| deca | da | 10 | 101 | ten |
| — | — | 1 | 100 | one |
| deci | d | 0.1 | 10−1 | tenth |
| centi | c | 0.01 | 10−2 | hundredth |
| milli | m | 0.001 | 10−3 | thousandth |
| micro | μ | 0.000001 | 10−6 | millionth |
| nano | n | 0.000000001 | 10−9 | billionth |
| pico | p | 0.000000000001 | 10−12 | trillionth |
| femto | f | 0.000000000000001 | 10−15 | quadrillionth |

## Units of Mass, Volume, and Length

The units of measurement you will encounter most frequently in chemistry are those for mass, volume, and length. The basic SI unit for mass is the kilogram (kg), but in the laboratory, mass is usually expressed in either grams (g) or milligrams (mg): 1000 g = 1 kg, 1000 mg = 1 g, and 1,000,000 mg = 1 kg. Units for volume are derived from the cube of the SI unit for length, which is the meter (m). Thus the basic SI unit for volume is cubic meters (length × width × height = $m^3$). In chemistry, however, volumes are usually reported in cubic centimeters ($cm^3$) and cubic decimeters ($dm^3$) or milliliters (mL) and liters (L), although the liter is not an SI unit of measurement. The relationships between these units are as follows:

$$1L = 1000mL = 1dm^3 \tag{1.10.1}$$

$$1mL = 1cm^3 \tag{1.10.2}$$

$$1000cm^3 = 1L \tag{1.10.3}$$

## Scientific Notation

Chemists often work with numbers that are exceedingly large or small. For example, entering the mass in grams of a hydrogen atom into a calculator requires a display with at least 24 decimal places. A system called scientific notation avoids much of the tedium and awkwardness of manipulating numbers with large or small magnitudes. In scientific notation, these numbers are expressed in the form

$$N \times 10^n \tag{1.10.4}$$

where N is greater than or equal to 1 and less than 10 ($1 \le N < 10$), and n is a positive or negative integer ($10^0 = 1$). The number 10 is called the base because it is this number that is raised to the power n. Although a base number may have values other than 10, the base number in scientific notation is always 10.

A simple way to convert numbers to scientific notation is to move the decimal point as many places to the left or right as needed to give a number from 1 to 10 (N). The magnitude of n is then determined as follows:

- If the decimal point is moved to the left n places, n is positive.
- If the decimal point is moved to the right n places, n is negative.

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Skill Builder ES1.

**Skill Builder ES1**

Convert each number to scientific notation.

a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.00032
f. 61.06700
g. 2002.080
h. 0.01020

**SOLUTION**

a. To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left:
637.8
Because the decimal point was moved two places to the left, n = 2. In scientific notation, $637.8 = 6.378 \times 10^2$.

b. To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right:
0.0479
Because the decimal point was moved two places to the right, n = −2. In scientific notation, $0.0479 = 4.79 \times 10^{-2}$.

c. $7.86 \times 10^0$: this is usually expressed simply as 7.86. (Recall that $10^0 = 1$.)

d. $1.2378 \times 10^4$; because the decimal point was moved four places to the left, n = 4.

e. $3.2 \times 10^{-4}$; because the decimal point was moved four places to the right, n = −4.

f. $6.106700 \times 10^1$: this is usually expressed as $6.1067 \times 10$.

g. $2.002080 \times 10^3$

h. $1.020 \times 10^{-2}$

## Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Skill Builder ES2 illustrates how to do this.

**Skill Builder ES2**

Carry out the appropriate operation on each number and then express the answer in scientific notation.

a. $(1.36 \times 10^2) + (4.73 \times 10^3)$

b. $(6.923 \times 10^{-3}) - (8.756 \times 10^{-4})$

**SOLUTION**

a. Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^2) + (47.3 \times 10^2)$ or $(0.136 \times 10^3) + (4.73 \times 10^3)$. Choosing either alternative gives the same answer, reported to two decimal places:

$(1.36 \times 10^2) + (47.3 \times 10^2) = (1.36 + 47.3) \times 10^2 = 48.66 \times 10^2 = 4.87 \times 10^3$

$(0.136 \times 10^3) + (4.73 \times 10^3) = (0.136 + 4.73) \times 10^3 = 4.87 \times 10^3$

In converting $48.66 \times 10^2$ to scientific notation, n has become more positive by 1 because the value of N has decreased.

b. Converting the exponents to the same value gives either $(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3})$ or $(69.23 \times 10^{-4}) - (8.756 \times 10^{-4})$. Completing the calculations gives the same answer, expressed to three decimal places:

$(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) = (6.923 - 0.8756) \times 10^{-3} = 6.047 \times 10^{-3}$

$(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) = (69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4} = 6.047 \times 10^{-3}$

## Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n. Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Skill Builder ES3.

**Skill Builder ES3**

Perform the appropriate operation on each expression and express your answer in scientific notation.

a. $(6.022 \times 10^{23})(6.42 \times 10^{-2})$

b. $\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}}$

c. $\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{8.52 \times 10^{-2}}$

Solution

a. In multiplication, we add the exponents:

$$(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21} = 3.87 \times 10^{22}$$

b. In division, we subtract the exponents:

$$\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^4 = 1.83 \times 10^3$$

c. This problem has both multiplication and division:

$$\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]} = 4.7 \times 10^{-31} \qquad (1.10.5)$$

## Significant Figures

No measurement is free from error. Error is introduced by (1) the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and (2) the imperfection of human senses. Although errors in calculations can be enormous, they do not contribute to uncertainty in measurements. Chemists describe the estimated degree of error in a measurement as the uncertainty of the measurement, and they are careful to report all measured values using only significant figures, numbers that describe the value without exaggerating the degree to which it is known to be accurate. Chemists report as

significant all numbers known with absolute certainty, plus one more digit that is understood to contain some uncertainty. The uncertainty in the final digit is usually assumed to be ±1, unless otherwise stated.

The following rules have been developed for counting the number of significant figures in a measurement or calculation:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits are significant. The number 2005, for example, has four significant figures.
3. Any zeros used as a placeholder preceding the first nonzero digit are not significant. So 0.05 has one significant figure because the zeros are used to indicate the placement of the digit 5. In contrast, 0.050 has two significant figures because the last two digits correspond to the number 50; the last zero is not a placeholder. As an additional example, 5.0 has two significant figures because the zero is used not to place the 5 but to indicate 5.0.
4. When a number does not contain a decimal point, zeros added after a nonzero number may or may not be significant. An example is the number 100, which may be interpreted as having one, two, or three significant figures. (Note: treat all trailing zeros in exercises and problems in this text as significant unless you are specifically told otherwise.)
5. Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000…). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

$$1ft = 12in \tag{1.10.6}$$

An effective method for determining the number of significant figures is to convert the measured or calculated value to scientific notation because any zero used as a placeholder is eliminated in the conversion. When 0.0800 is expressed in scientific notation as $8.00 \times 10^{-2}$, it is more readily apparent that the number has three significant figures rather than five; in scientific notation, the number preceding the exponential (i.e., N) determines the number of significant figures. Skill Builder ES4 provides practice with these rules.

Skill Builder ES4

Give the number of significant figures in each. Identify the rule for each.

a. 5.87
b. 0.031
c. 52.90
d. 00.2001
e. 500
f. 6 atoms

**Solution**

a. three (rule 1)
b. two (rule 3); in scientific notation, this number is represented as $3.1 \times 10^{-2}$, showing that it has two significant figures.
c. four (rule 3)
d. four (rule 2); this number is $2.001 \times 10^{-1}$ in scientific notation, showing that it has four significant figures.
e. one, two, or three (rule 4)
f. infinite (rule 5)

Skill Builder ES5

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?




**Solution**

Use the 10 mL graduated cylinder, which will be accurate to two significant figures.

Mathematical operations are carried out using all the digits given and then rounding the final result to the correct number of significant figures to obtain a reasonable answer. This method avoids compounding inaccuracies by successively rounding intermediate calculations. After you complete a calculation, you may have to round the last significant figure up or down depending on the value of the digit that follows it. If the digit is 5 or greater, then the number is rounded up. For example, when rounded to three significant figures, 5.215 is 5.22, whereas 5.213 is 5.21. Similarly, to three significant figures, 5.005 kg becomes 5.01 kg, whereas 5.004 kg becomes 5.00 kg. The procedures for dealing with significant figures are different for addition and subtraction versus multiplication and division.

When we add or subtract measured values, the value with the fewest significant figures to the right of the decimal point determines the number of significant figures to the right of the decimal point in the answer. Drawing a vertical line to the right of the column corresponding to the smallest number of significant figures is a simple method of determining the proper number of significant figures for the answer:

| | |
|---|---|
| 3240.7<br>+ 21.2 | 36 |
| 3261.9 | 36 |

The line indicates that the digits 3 and 6 are not significant in the answer. These digits are not significant because the values for the corresponding places in the other measurement are unknown (3240.7??). Consequently, the answer is expressed as 3261.9, with five significant figures. Again, numbers greater than or equal to 5 are rounded up. If our second number in the calculation had been 21.256, then we would have rounded 3261.956 to 3262.0 to complete our calculation.

When we multiply or divide measured values, the answer is limited to the smallest number of significant figures in the calculation; thus, 42.9 × 8.323 = 357.057 = 357. Although the second number in the calculation has four significant figures, we are justified in reporting the answer to only three significant figures because the first number in the calculation has only three significant figures. An exception to this rule occurs when multiplying a number by an integer, as in 12.793 × 12. In this case, the number of significant figures in the answer is determined by the number 12.973, because we are in essence adding 12.973 to itself 12 times. The correct answer is therefore 155.516, an increase of one significant figure, not 155.52.

When you use a calculator, it is important to remember that the number shown in the calculator display often shows more digits than can be reported as significant in your answer. When a measurement reported as 5.0 kg is divided by 3.0 L, for example, the display may show 1.666666667 as the answer. We are justified in reporting the answer to only two significant figures, giving 1.7 kg/L as the answer, with the last digit understood to have some uncertainty.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should always be performed at the end of a series of calculations because rounding of intermediate results can sometimes cause the final answer to be significantly in error.

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate roundings need to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step. Skill Builder ES6 provides practice with calculations using significant figures.

Skill Builder ES6

Complete the calculations and report your answers using the correct number of significant figures.

a. 87.25 mL + 3.0201 mL
b. 26.843 g + 12.23 g
c. 6 × 12.011
d. 2(1.008) g + 15.99 g
e. 137.3 + 2(35.45)
f. $\frac{118.7}{2}g - 35.5g$
g. $47.23g - \frac{207.2}{5.92}g$
h. $\frac{77.604}{6.467} - 4.8$
i. $\frac{24.86}{2.0} - 3.26(0.98)$
j. $(15.9994 \times 9) + 2.0158$

**Solution**

a. 90.27 mL
b. 39.07 g
c. 72.066 (See rule 5 under “Significant Figures.”)
d. 2(1.008) g + 15.99 g = 2.016 g + 15.99 g = 18.01 g
e. 137.3 + 2(35.45) = 137.3 + 70.90 = 208.2
f. 59.35 g − 35.5 g = 23.9 g
g. 47.23 g − 35.0 g = 12.2 g
h. 12.00 − 4.8 = 7.2
i. 12 − 3.2 = 9
j. 143.9946 + 2.0158 = 146.0104

## Accuracy and Precision

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

Suppose, for example, that the mass of a sample of gold was measured on one balance and found to be 1.896 g. On a different balance, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on a calibrated third balance, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

| Balance 1 | Balance 2 | Balance 3 |
|---|---|---|
| 1.896 g | 1.125 g | 1.893 g |
| 1.895 g | 1.158 g | 1.895 g |
| 1.894 g | 1.067 g | 1.895 g |

Whereas the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), those obtained from balance 2 are neither. Even if the measurements obtained from balance 2 had been precise (if, for example, they had been 1.125, 1.124, and 1.125), they still would not have been accurate. We can assess the precision of a set of measurements by calculating the average deviation of the measurements as follows:

1. Calculate the average value of all the measurements:

$$average = \frac{sum of measurements}{number of measurements} \tag{1.10.7}$$

2. Calculate the deviation of each measurement, which is the absolute value of the difference between each measurement and the average value:

deviation = |measurement − average|

where | | means absolute value (i.e., convert any negative number to a positive number).

3. Add all the deviations and divide by the number of measurements to obtain the average deviation:

\[ average = {sum of deviations \over number of measurements} \]

Then we can express the precision as a percentage by dividing the average deviation by the average value of the measurements and multiplying the result by 100. In the case of balance 2, the average value is

$$\frac{1.125g + 1.158 + 1.067g}{3} = 1.117g \tag{1.10.8}$$

The deviations are 1.125 g − 1.117 g = 0.008 g, 1.158 g − 1.117 g = 0.041 g, and |1.067 g − 1.117 g| = 0.050 g. So the average deviation is

$$\frac{0.008g + 0.041g + 0.050g}{3} = 0.033g \tag{1.10.9}$$

The precision of this set of measurements is therefore

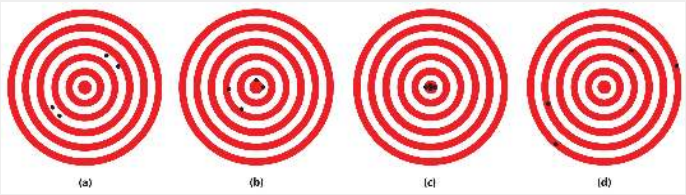
$$\frac{0.033g}{1.117g} \times 100 = 3.0\% \tag{1.10.10}$$

When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique. The difference between accuracy and precision is demonstrated in Skill Builder ES7.

Skill Builder ES7

The following archery targets show marks that represent the results of four sets of measurements. Which target shows

a. a precise but inaccurate set of measurements?
b. an accurate but imprecise set of measurements?
c. a set of measurements that is both precise and accurate?
d. a set of measurements that is neither precise nor accurate?




SOLUTION

a. (c)
b. (a)
c. (b)
d. (d)

Skill Builder ES8

a. A 1-carat diamond has a mass of 200.0 mg. When a jeweler repeatedly weighed a 2-carat diamond, he obtained measurements of 450.0 mg, 459.0 mg, and 463.0 mg. Were the jeweler's measurements accurate? Were they precise?
b. A single copper penny was tested three times to determine its composition. The first analysis gave a composition of 93.2% zinc
and 2.8% copper, the second gave 92.9% zinc and 3.1% copper, and the third gave 93.5% zinc and 2.5% copper. The actual composition of the penny was 97.6% zinc and 2.4% copper. Were the results accurate? Were they precise?

**SOLUTION**

a. The expected mass of a 2-carat diamond is 2 × 200.0 mg = 400.0 mg. The average of the three measurements is 457.3 mg, about 13% greater than the true mass. These measurements are not particularly accurate.
The deviations of the measurements are 7.3 mg, 1.7 mg, and 5.7 mg, respectively, which give an average deviation of 4.9 mg and a precision of

$$\frac{4.9mg}{457.3mg} \times 100 = 1.1\% \tag{1.10.11}$$

These measurements are rather precise.
b. The average values of the measurements are 93.2% zinc and 2.8% copper versus the true values of 97.6% zinc and 2.4% copper. Thus these measurements are not very accurate, with errors of −4.5% and + 17% for zinc and copper, respectively. (The sum of the measured zinc and copper contents is only 96.0% rather than 100%, which tells us that either there is a significant error in one or both measurements or some other element is present.)
The deviations of the measurements are 0.0%, 0.3%, and 0.3% for both zinc and copper, which give an average deviation of 0.2% for both metals. We might therefore conclude that the measurements are equally precise, but that is not the case. Recall that precision is the average deviation divided by the average value times 100. Because the average value of the zinc measurements is much greater than the average value of the copper measurements (93.2% versus 2.8%), the copper measurements are much less precise.

$$\text{precision (Zn)} = \frac{0.2\%}{93.2\%} \times 100 = 0.2\% \tag{1.10.12}$$

$$\text{precision (Cu)} = \frac{0.2\%}{2.8\%} \times 100 = 7\% \tag{1.10.13}$$

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# CHAPTER OVERVIEW

## 2: Molecules, Ions, and Chemical Formulas


2.1: Chemical Compounds
2.2: Chemical Formulas
2.3: Naming Ionic Compounds
2.4: Naming Covalent Compounds
2.5: Acids and Bases
2.6: Industrially Important Chemicals


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# 2.1: Chemical Compounds

**Learning Objectives**

- To understand the differences between covalent and ionic bonding.

The atoms in all substances that contain more than one atom are held together by **electrostatic interactions**—interactions between electrically charged particles such as protons and electrons. **Electrostatic attraction** between oppositely charged species (positive and negative) results in a force that causes them to move toward each other, like the attraction between opposite poles of two magnets. In contrast, **electrostatic repulsion** between two species with the same charge (either both positive or both negative) results in a force that causes them to repel each other, as do the same poles of two magnets. Atoms form chemical compounds when the attractive electrostatic interactions between them are stronger than the repulsive interactions. Collectively, we refer to the attractive interactions between atoms as **chemical bonds**.

Chemical bonds are generally divided into two fundamentally different kinds: ionic and covalent. In reality, however, the bonds in most substances are neither purely ionic nor purely covalent, but they are closer to one of these extremes. Although purely ionic and purely covalent bonds represent extreme cases that are seldom encountered in anything but very simple substances, a brief discussion of these two extremes helps us understand why substances that have different kinds of chemical bonds have very different properties. **Ionic compounds** consist of positively and negatively charged ions held together by strong electrostatic forces, whereas **covalent compounds** generally consist of **molecules**, which are groups of atoms in which one or more pairs of electrons are shared between bonded atoms. In a **covalent bond**, the atoms are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share. We begin our discussion of structures and formulas by describing covalent compounds. The energetic factors involved in bond formation are described in more quantitative detail in Chapter 8.

### Note the Pattern

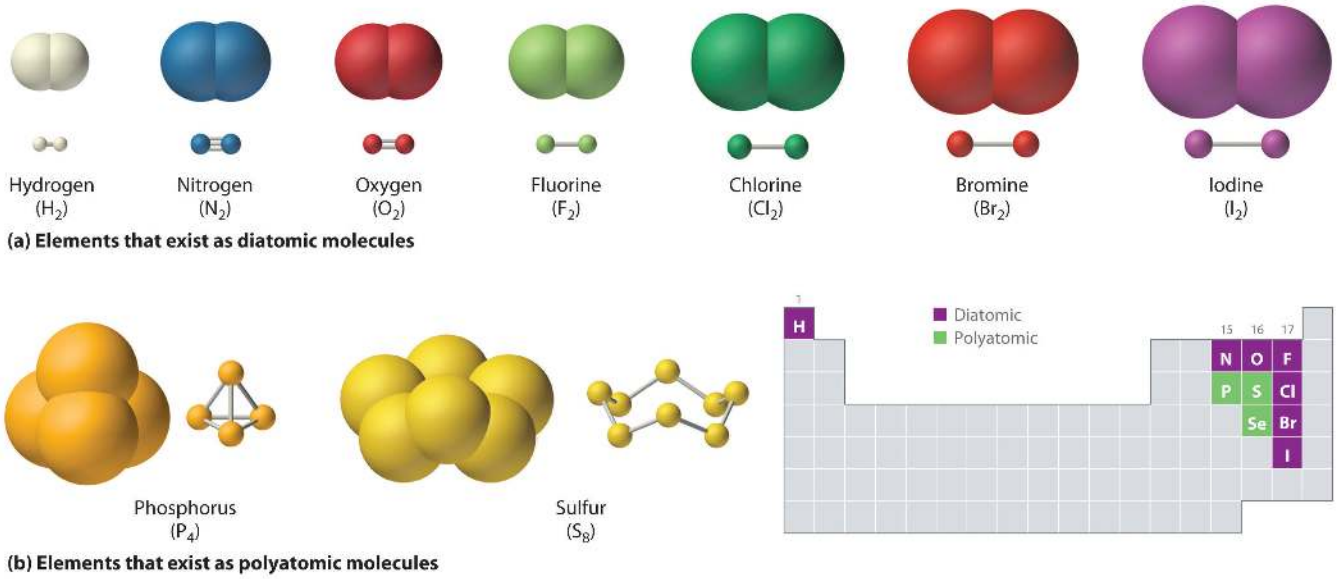
Ionic compounds consist of ions of opposite charges held together by strong electrostatic forces, whereas pairs of electrons are shared between bonded atoms in covalent compounds.

## Covalent Molecules and Compounds

Just as an atom is the simplest unit that has the fundamental chemical properties of an element, a molecule is the simplest unit that has the fundamental chemical properties of a covalent compound. Some pure elements exist as covalent molecules. Hydrogen, nitrogen, oxygen, and the halogens occur naturally as the *diatomic* (“two atoms”) *molecules* $H_2$, $N_2$, $O_2$, $F_2$, $Cl_2$, $Br_2$, and $I_2$ (part (a) in Figure 2.1.1. Similarly, a few pure elements are **polyatomic** (“many atoms”) *molecules*, such as elemental phosphorus and sulfur, which occur as $P_4$ and $S_8$ (part (b) in Figure 2.1.1.

Each covalent compound is represented by a **molecular formula**, which gives the atomic symbol for each component element, in a prescribed order, accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number of atoms is greater than 1. For example, water, with two hydrogen atoms and one oxygen atom per molecule, is written as $H_2O$. Similarly, carbon dioxide, which contains one carbon atom and two oxygen atoms in each molecule, is written as $CO_2$.

Figure 2.1.1 *Elements That Exist as Covalent Molecules*




*(a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula $E_2$. (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as $P_4$ tetrahedra—regular polyhedra with four triangular sides—with a phosphorus atom at each vertex. Elemental sulfur consists of a puckered ring of eight sulfur atoms connected by single bonds. Selenium is not shown due to the complexity of its structure.*

Covalent compounds that contain predominantly carbon and hydrogen are called **organic compounds**. The convention for representing the formulas of organic compounds is to write carbon first, followed by hydrogen and then any other elements in alphabetical order (e.g., $CH_4O$ is methyl alcohol, a fuel). Compounds that consist primarily of elements other than carbon and hydrogen are called **inorganic compounds**; they include both covalent and ionic compounds. In inorganic compounds, the component elements are listed beginning with the one farthest to the left in the periodic table , such as we see in $CO_2$ or $SF_6$. Those in the same group are listed beginning with the lower element and working up, as in ClF. By convention, however, when an inorganic compound contains both hydrogen and an element from groups 13–15, the hydrogen is usually listed last in the formula. Examples are ammonia ($NH_3$) and silane ($SiH_4$). Compounds such as water, whose compositions were established long before this convention was adopted, are always written with hydrogen first: Water is always written as $H_2O$, not $OH_2$. The conventions for inorganic acids, such as hydrochloric acid (HCl) and sulfuric acid ($H_2SO_4$), are described in Section 2.5.

### Note the Pattern

For organic compounds: write C first, then H, and then the other elements in alphabetical order. For molecular inorganic compounds: start with the element at far left in the periodic table; list elements in same group beginning with the lower element and working up.

### ✔ Example 2.1.1

Write the molecular formula of each compound.

1. The phosphorus-sulfur compound that is responsible for the ignition of so-called strike anywhere matches has 4 phosphorus atoms and 3 sulfur atoms per molecule.
2. Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
3. Freon-11, once widely used in automobile air conditioners and implicated in damage to the ozone layer, has 1 carbon atom, 3 chlorine atoms, and 1 fluorine atom per molecule.

**Given:** identity of elements present and number of atoms of each

**Asked for:** molecular formula

**Strategy:**

**A** Identify the symbol for each element in the molecule. Then identify the substance as either an organic compound or an inorganic compound.

**B** If the substance is an organic compound, arrange the elements in order beginning with carbon and hydrogen and then list the other elements alphabetically. If it is an inorganic compound, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up.

**C** From the information given, add a subscript for each kind of atom to write the molecular formula.

**A** Identify the symbol for each element in the molecule. Then identify the substance as either an organic compound or an inorganic compound.

**B** If the substance is an organic compound, arrange the elements in order beginning with carbon and hydrogen and then list the other elements alphabetically. If it is an inorganic compound, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up.

**C** From the information given, add a subscript for each kind of atom to write the molecular formula.

**Solution**

1. **A** The molecule has 4 phosphorus atoms and 3 sulfur atoms. Because the compound does not contain mostly carbon and hydrogen, it is inorganic. **B** Phosphorus is in group 15, and sulfur is in group 16. Because phosphorus is to the left of sulfur, it is written first. **C** Writing the number of each kind of atom as a right-hand subscript gives $P_4S_3$ as the molecular formula.
2. **A** Ethyl alcohol contains predominantly carbon and hydrogen, so it is an organic compound. **B** The formula for an organic compound is written with the number of carbon atoms first, the number of hydrogen atoms next, and the other atoms in alphabetical order: CHO. **C** Adding subscripts gives the molecular formula $C_2H_6O$.
3. **A** Freon-11 contains carbon, chlorine, and fluorine. It can be viewed as either an inorganic compound or an organic compound (in which fluorine has replaced hydrogen). The formula for Freon-11 can therefore be written using either of the two conventions.

   **B** According to the convention for inorganic compounds, carbon is written first because it is farther left in the periodic table. Fluorine and chlorine are in the same group, so they are listed beginning with the lower element and working up: CClF. Adding subscripts gives the molecular formula $CCl_3F$.

   **C** We obtain the same formula for Freon-11 using the convention for organic compounds. The number of carbon atoms is written first, followed by the number of hydrogen atoms (zero) and then the other elements in alphabetical order, also giving $CCl_3F$.

## ? Exercise 2.1.1

Write the molecular formula for each compound.

1. Nitrous oxide, also called “laughing gas,” has 2 nitrogen atoms and 1 oxygen atom per molecule. Nitrous oxide is used as a mild anesthetic for minor surgery and as the propellant in cans of whipped cream.
2. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.
3. Sulfur hexafluoride, a gas used to pressurize “unpressurized” tennis balls and as a coolant in nuclear reactors, has 6 fluorine atoms and 1 sulfur atom per molecule.

**Answer**

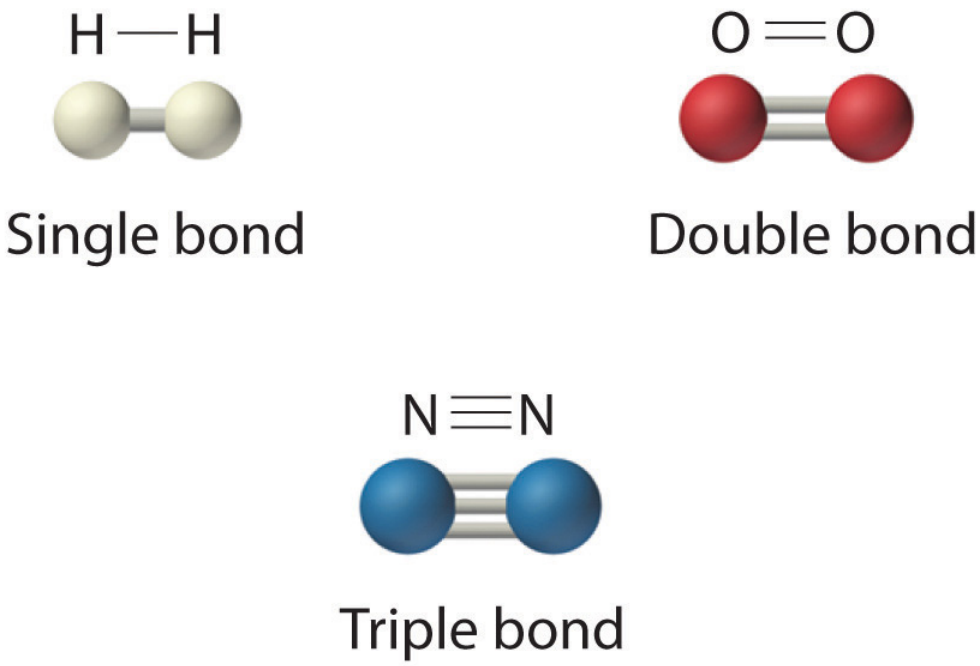
1. $N_2O$
2. $C_{12}H_{22}O_{11}$
3. $SF_6$

## Representations of Molecular Structures

Molecular formulas give only the elemental composition of molecules. In contrast, **structural formulas** show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

The structural formula for $H_2$ can be drawn as H–H and that for $I_2$ as I–I, where the line indicates a single pair of shared electrons, a **single bond**. Two pairs of electrons are shared in a **double bond**, which is indicated by two lines— for example, $O_2$ is O=O. Three electron pairs are shared in a **triple bond**, which is indicated by three lines—for example, $N_2$ is N≡N (see Figure 2.1.2. Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is *not* arbitrary. As you will learn in Chapter 8, hydrogen, oxygen, nitrogen, and carbon have a very strong tendency to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table 2.1.1.

Figure 2.1.2 *Molecules That Contain Single, Double, and Triple Bonds*

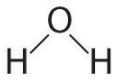



*Hydrogen ($H_2$) has a single bond between atoms. Oxygen ($O_2$) has a double bond between atoms, indicated by two lines (=). Nitrogen ($N_2$) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron pair.*

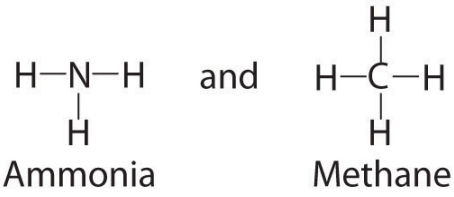
Tabl 2.1.1 The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

| Atom | Number of Bonds |
|---|---|
| H (group 1) | 1 |
| O (group 16) | 2 |
| N (group 15) | 3 |
| C (group 14) | 4 |

The structural formula for water can be drawn as follows:

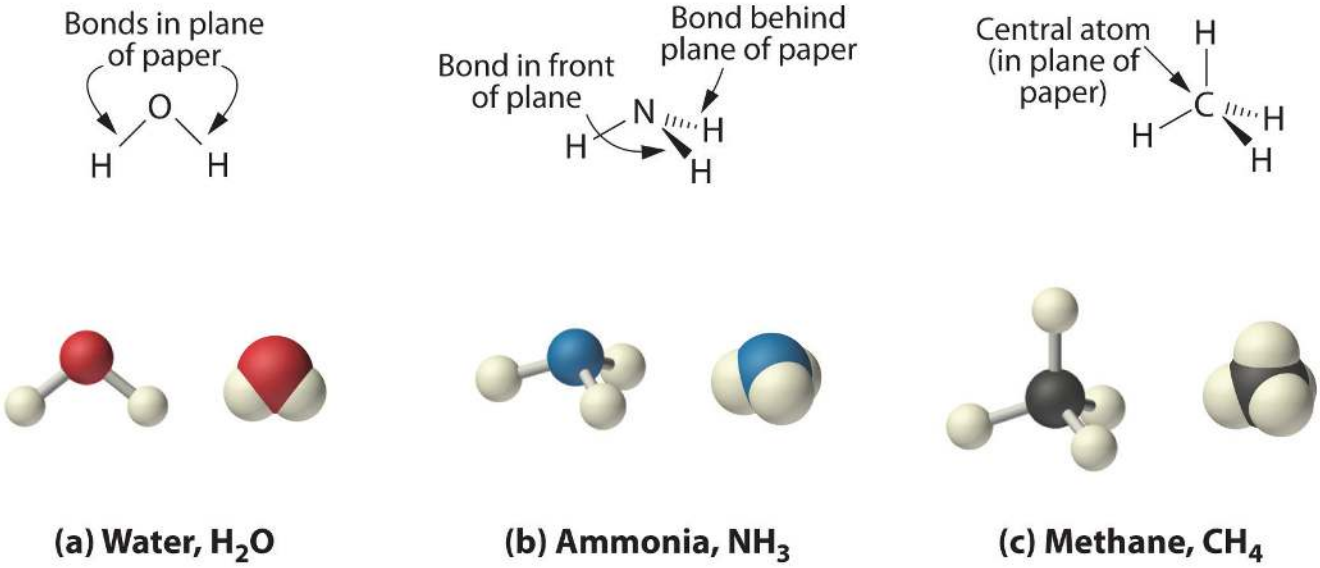


Because the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia ($NH_3$) and methane ($CH_4$) are often written as planar molecules:

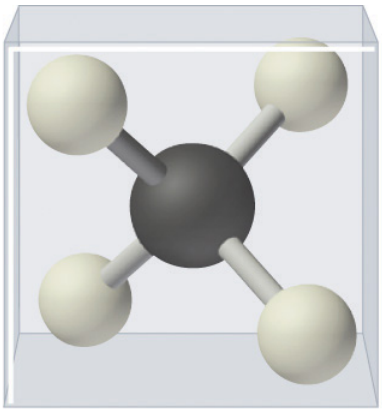



As shown in Figure 2.1.3, however, the actual three-dimensional structure of $NH_3$ looks like a pyramid with a triangular base of three hydrogen atoms. The structure of $CH_4$, with four hydrogen atoms arranged around a central carbon atom as shown in Figure 2.1.3, is *tetrahedral*. That is, the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.

Figure 2.1.3 *The Three-Dimensional Structures of Water, Ammonia, and Methane*




*(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*

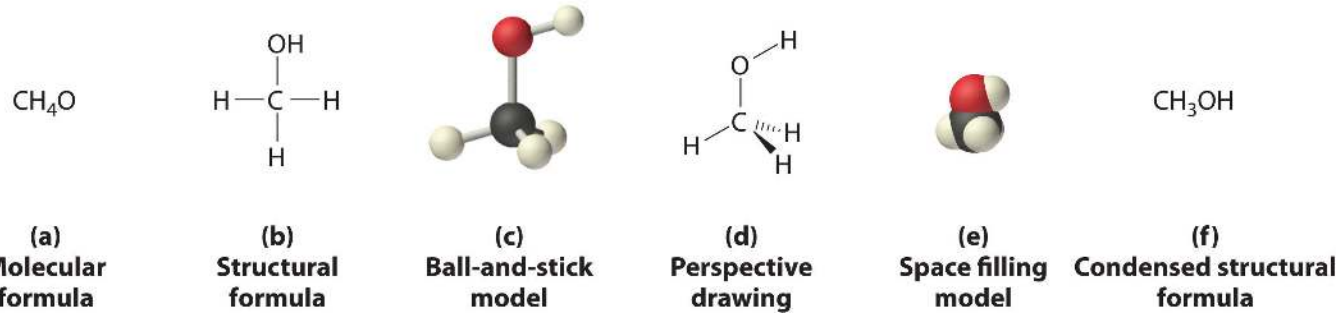


Tetrahedral structure of methane, $CH_4$

***$CH_4$.*** *Methane has a three-dimensional, tetrahedral structure.*

Figure 2.1.1, Figure 2.1.2, and Figure 2.1.3 illustrate different ways to represent the structures of molecules. It should be clear that there is no single "best" way to draw the structure of a molecule; the method you use depends on which aspect of the structure you want to emphasize and how much time and effort you want to spend. Figure 2.1.4 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (part (a) in Figure 2.1.4) gives only the number of each kind of atom; writing methanol as $CH_4O$ tells nothing about its structure. In contrast, the structural formula (part (b) in Figure 2.1.4) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 2.1.4) and the perspective drawing (part (d) in Figure 2.1.4) show the three-dimensional structure of the molecule. The latter (also called a *wedge-and-dash* representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 2.1.4) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. Also, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

Figure 2.1.4*Different Ways of Representing the Structure of a Molecule*




*(a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.*

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a *condensed structural formula* (part (f) in Figure 2.1.4), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is $CH_3OH$, which tells us that the molecule contains a $CH_3$ unit that looks like a fragment of methane ($CH_4$). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

### Example 2.1.1

1. Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl.
2. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
3. Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(CH_3)_3N$.

**Given:** condensed structural formula

**Asked for:** molecular formula

**Strategy:**

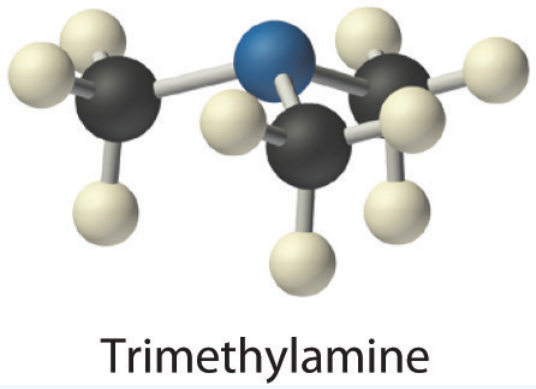
**A** Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.

**B** As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

**Solution**

The molecular formula lists the elements in the molecule and the number of atoms of each.

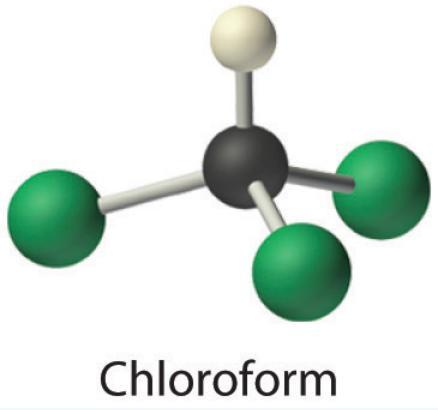
1. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula $S_2Cl_2$.
2. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.
3. **A** The condensed structural formula shows that trimethylamine contains three $CH_3$ units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula $C_3H_9N$.




**? Exercise 2.1.1**

Write the molecular formula for each molecule.

1. Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms. Its condensed structural formula is $CHCl_3$.
2. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is $H_2NNH_2$.
3. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is $H_2NCH_2CH_2CH_2CH_2NH_2$. This is often written as $H_2N(CH_2)_4NH_2$ to indicate that there are four $CH_2$ fragments linked together.




**Answer**

1. $CHCl_3$
2. $N_2H_4$
3. $C_4H_{12}N_2$

## Ionic Compounds

The substances described in the preceding discussion are composed of molecules that are electrically neutral; that is, the number of positively charged protons in the nucleus is equal to the number of negatively charged electrons. In contrast, *ions* are atoms or assemblies of atoms that have a net electrical charge. Ions that contain fewer electrons than protons have a net positive charge and are called **cations**. Conversely, ions that contain more electrons than protons have a net negative charge and are called **anions**. *Ionic compounds* contain both cations and anions in a ratio that results in no net electrical charge.

### Note the Pattern

Ionic compounds contain both cations and anions in a ratio that results in zero electrical charge.

In covalent compounds, electrons are shared between bonded atoms and are simultaneously attracted to more than one nucleus. In contrast, ionic compounds contain cations and anions rather than discrete neutral molecules. Ionic compounds are held together by the attractive electrostatic interactions between cations and anions. In an ionic compound, the cations and anions are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 2.1.5). As shown in Equation 2.1, the electrostatic energy of the interaction between two charged particles is proportional to the product of the charges on the particles and inversely proportional to the distance between them:

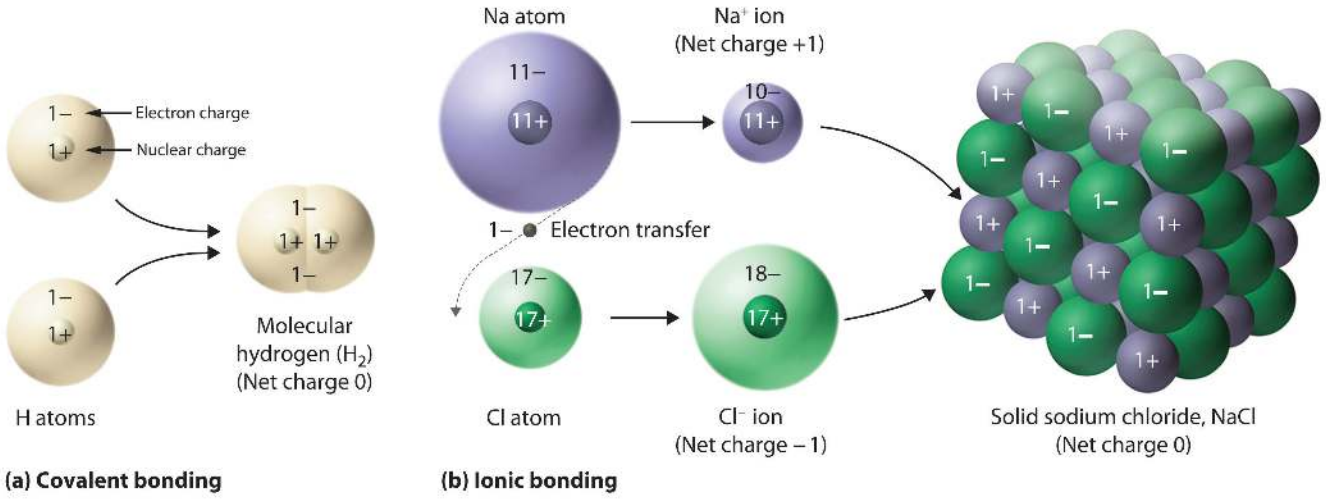
$$electrostatic\ energy = \alpha \frac{Q_1 Q_2}{r} \tag{2.1.1}$$

where $Q_1$ and $Q_2$ are the electrical charges on particles 1 and 2, and $r$ is the distance between them. When $Q_1$ and $Q_2$ are both positive, corresponding to the charges on cations, the cations repel each other and the electrostatic energy is positive. When $Q_1$ and $Q_2$ are both negative, corresponding to the charges on anions, the anions repel each other and the electrostatic energy is again positive. The electrostatic energy is negative only when the charges have opposite signs; that is, positively charged species are attracted to negatively charged species and vice versa. As shown in Figure 2.1.6, the strength of the interaction is proportional to the *magnitude* of the charges and decreases as the *distance* between the particles increases. We will return to these energetic factors in Chapter 8, where they are described in greater quantitative detail.

## Note the Pattern

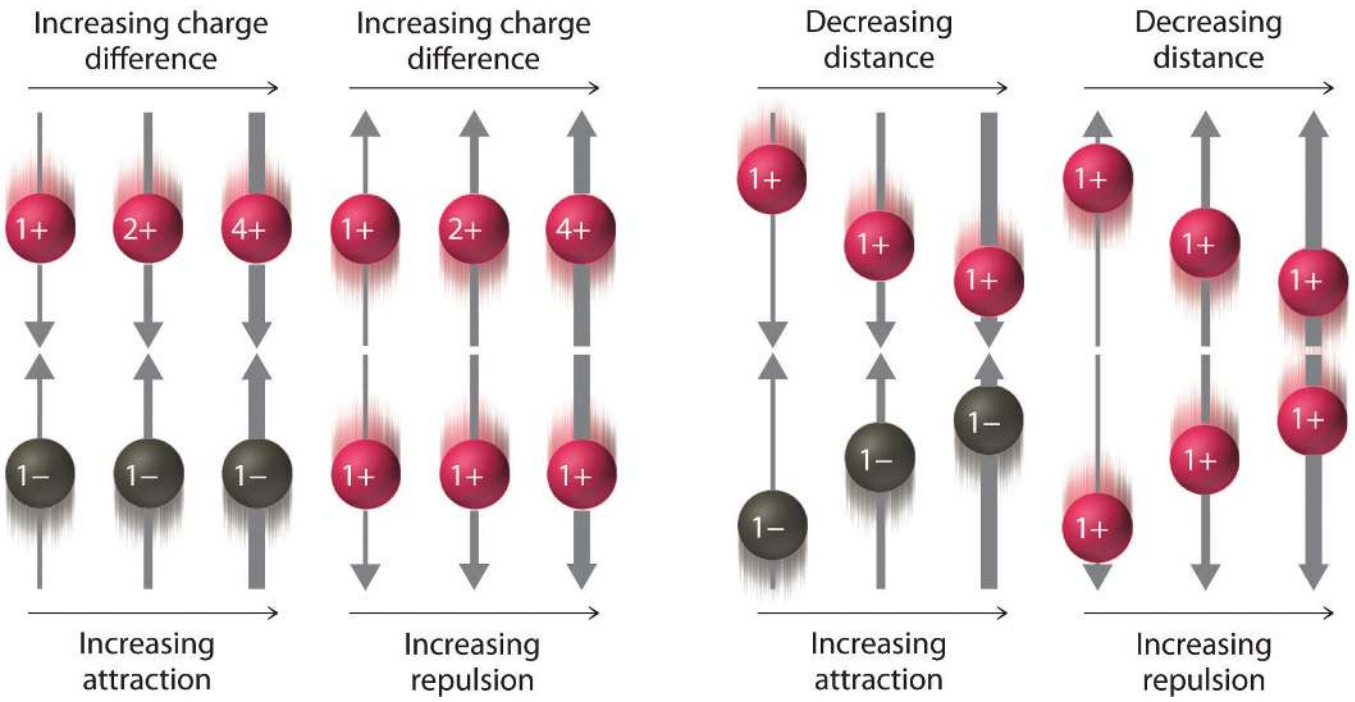
If the electrostatic energy is positive, the particles repel each other; if the electrostatic energy is negative, the particles are attracted to each other.

Figure 2.1.5 *Covalent and Ionic Bonding*




*(a) In molecular hydrogen ($H_2$), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting $Na^+$ and $Cl^-$ ions form a three-dimensional solid that is held together by attractive electrostatic interactions.*

Figure 2.1.6 *The Effect of Charge and Distance on the Strength of Electrostatic Interactions*

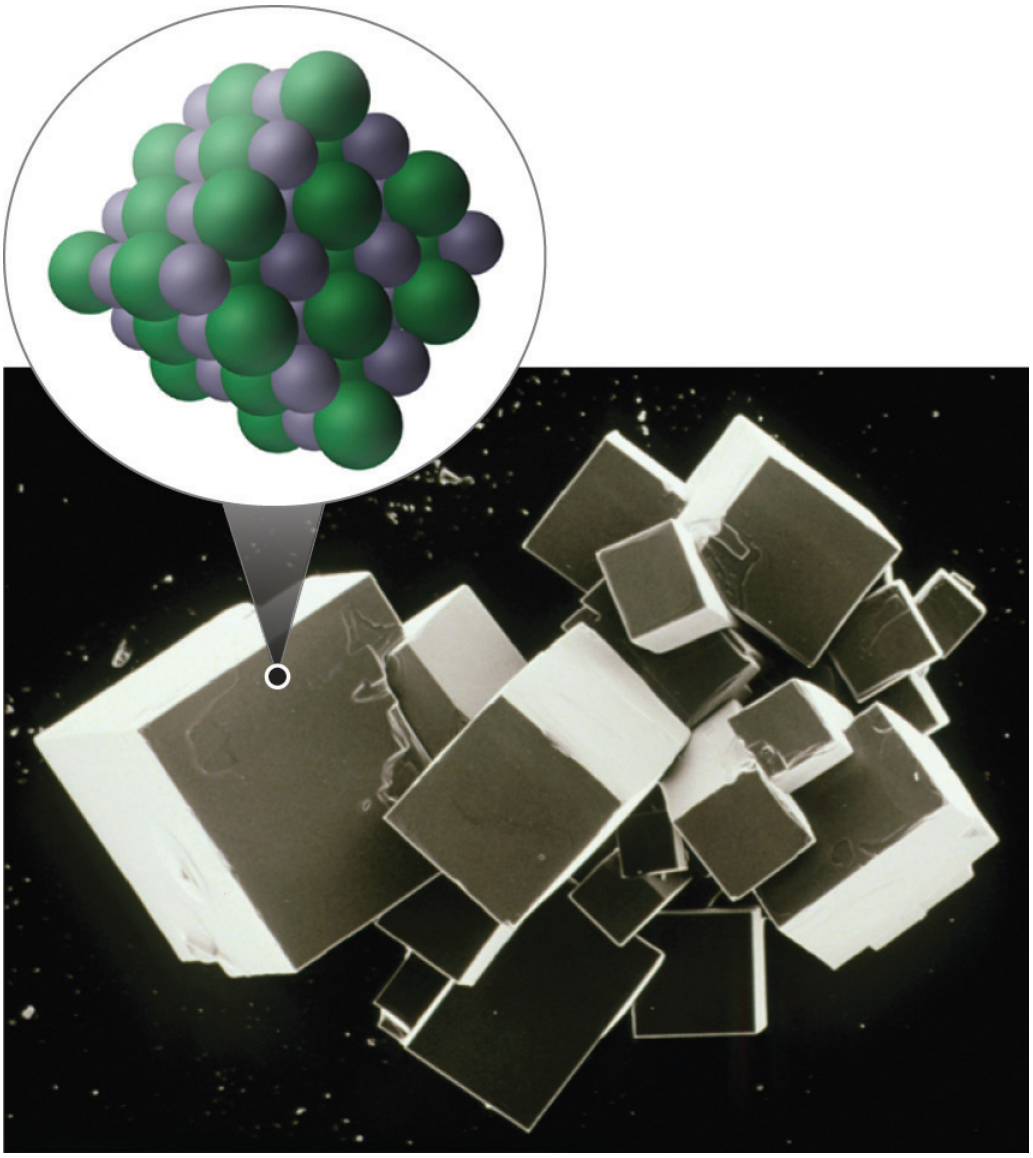



*As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (−…+) or repulsive (−…− or +…+) interactions. The strength of these interactions is represented by the thickness of the arrows.*

One example of an ionic compound is sodium chloride (NaCl; Figure 2.1.7), formed from sodium and chlorine. In forming chemical compounds, many elements have a tendency to gain or lose enough electrons to attain the same number of electrons as the noble gas closest to them in the periodic table. When sodium and chlorine come into contact, each sodium atom gives up an electron to become a $Na^+$ ion, with 11 protons in its nucleus but only 10 electrons (like neon), and each chlorine atom gains an electron to become a $Cl^−$ ion, with 17 protons in its nucleus and 18 electrons (like argon), as shown in part (b) in Figure 2.1.5. Solid sodium chloride contains equal numbers of cations ($Na^+$) and anions ($Cl^−$), thus maintaining electrical neutrality. Each $Na^+$ ion is surrounded by 6 $Cl^−$ ions, and each $Cl^−$ ion is surrounded by 6 $Na^+$ ions. Because of the large number of attractive $Na^+Cl^−$ interactions, the total attractive electrostatic energy in NaCl is great.

Figure 2.1.7 *Sodium Chloride: an Ionic Solid*


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*The planes of an NaCl crystal reflect the regular three-dimensional arrangement of its $Na^+$ (purple) and $Cl^-$ (green) ions.*

Consistent with a tendency to have the same number of electrons as the nearest noble gas, when forming ions, elements in groups 1, 2, and 3 tend to *lose* one, two, and three electrons, respectively, to form cations, such as $Na^+$ and $Mg^{2+}$. They then have the same number of electrons as the nearest noble gas: neon. Similarly, $K^+$, $Ca^{2+}$, and $Sc^{3+}$ have 18 electrons each, like the nearest noble gas: argon. In addition, the elements in group 13 *lose* three electrons to form cations, such as $Al^{3+}$, again attaining the same number of electrons as the noble gas closest to them in the periodic table. Because the lanthanides and actinides formally belong to group 3, the most common ion formed by these elements is $M^{3+}$, where M represents the metal. Conversely, elements in groups 17, 16, and 15 often react to *gain* one, two, and three electrons, respectively, to form ions such as $Cl^-$, $S^{2-}$, and $P^{3-}$. Ions such as these, which contain only a single atom, are called **monatomic ions**. You can predict the charges of most monatomic ions derived from the main group elements by simply looking at the periodic table and counting how many columns an element lies from the extreme left or right. For example, you can predict that barium (in group 2) will form $Ba^{2+}$ to have the same number of electrons as its nearest noble gas, xenon, that oxygen (in group 16) will form $O^{2-}$ to have the same number of electrons as neon, and cesium (in group 1) will form $Cs^+$ to also have the same number of electrons as xenon. Note that this method does not usually work for most of the transition metals, as you will learn in Section 2.3. Some common monatomic ions are in Table 2.1.2

### Note the Pattern

Elements in groups 1, 2, and 3 tend to form 1+, 2+, and 3+ ions, respectively; elements in groups 15, 16, and 17 tend to form 3−, 2−, and 1− ions, respectively.

Table 2.1.2 Some Common Monatomic Ions and Their Names

| Group 1 | Group 2 | Group 3 | Group 13 | Group 15 | Group 16 | Group 17 |
|---|---|---|---|---|---|---|
| $Li^+$ lithium | $Be^{2+}$ beryllium | | | $N^{3-}$ nitride (azide) | $O^{2-}$ oxide | $F^-$ fluoride |
| $Na^+$ sodium | $Mg^{2+}$ magnesium | | $Al^{3+}$ aluminum | $P^{3-}$ phosphide | $S^{2-}$ sulfide | $Cl^-$ chloride |
| $K^+$ potassium | $Ca^{2+}$ calcium | $Sc^{3+}$ scandium | $Ga^{3+}$ gallium | $As^{3-}$ arsenide | $Se^{2-}$ selenide | $Br^-$ bromide |
| $Rb^+$ rubidium | $Sr^{2+}$ strontium | $Y^{3+}$ yttrium | $In^{3+}$ indium | | $Te^{2-}$ telluride | $I^-$ iodide |
| $Cs^+$ cesium | $Ba^{2+}$ barium | $La^{3+}$ lanthanum | | | | |

**Example 2.1.1**

Predict the charge on the most common monatomic ion formed by each element.

1. aluminum, used in the quantum logic clock, the world's most precise clock
2. selenium, used to make ruby-colored glass
3. yttrium, used to make high-performance spark plugs

**Given:** element

**Asked for:** ionic charge

**Strategy:**

**A** Identify the group in the periodic table to which the element belongs. Based on its location in the periodic table, decide whether the element is a metal, which tends to lose electrons; a nonmetal, which tends to gain electrons; or a semimetal, which can do either.

**B** After locating the noble gas that is closest to the element, determine the number of electrons the element must gain or lose to have the same number of electrons as the nearest noble gas.

**Solution**

1. **A** Aluminum is a metal in group 13; consequently, it will tend to lose electrons. **B** The nearest noble gas to aluminum is neon. Aluminum will lose three electrons to form the $Al^{3+}$ ion, which has the same number of electrons as neon.
2. **A** Selenium is a nonmetal in group 16, so it will tend to gain electrons. **B** The nearest noble gas is krypton, so we predict that selenium will gain two electrons to form the $Se^{2-}$ ion, which has the same number of electrons as krypton.
3. **A** Yttrium is in group 3, and elements in this group are metals that tend to lose electrons. **B** The nearest noble gas to yttrium is krypton, so yttrium is predicted to lose three electrons to form $Y^{3+}$, which has the same number of electrons as krypton.

**Exercise 2.1.1**

Predict the charge on the most common monatomic ion formed by each element.

1. calcium, used to prevent osteoporosis

2. iodine, required for the synthesis of thyroid hormones
3. zirconium, widely used in nuclear reactors

**Answer**

1. $Ca^{2+}$
2. $I^-$
3. $Zr^{4+}$

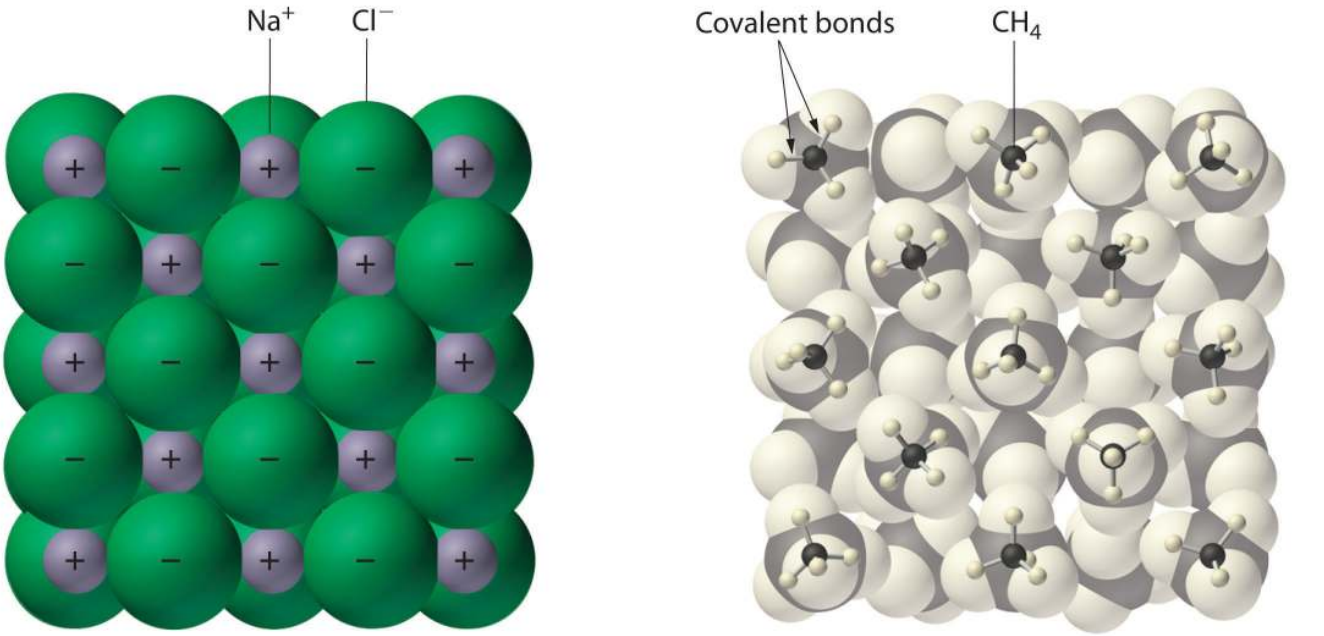
## Physical Properties of Ionic and Covalent Compounds

In general, ionic and covalent compounds have different physical properties. Ionic compounds usually form hard crystalline solids that melt at rather high temperatures and are *very* resistant to evaporation. These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in part (a) in Figure 2.1.8, which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions. In contrast, as shown in part (b) in Figure 2.1.8, most covalent compounds consist of discrete molecules held together by comparatively weak *intermolecular* forces (the forces between molecules), even though the atoms within each molecule are held together by strong *intramolecular* covalent bonds (the forces within the molecule). Covalent substances can be gases, liquids, or solids at room temperature and pressure, depending on the strength of the intermolecular interactions. Covalent molecular solids tend to form soft crystals that melt at rather low temperatures and evaporate relatively easily.Some covalent substances, however, are not molecular but consist of infinite three-dimensional arrays of covalently bonded atoms and include some of the hardest materials known, such as diamond. This topic will be addressed in Chapter 12. The covalent bonds that hold the atoms together in the molecules are unaffected when covalent substances melt or evaporate, so a liquid or vapor of discrete, independent molecules is formed. For example, at room temperature, methane, the major constituent of natural gas, is a gas that is composed of discrete $CH_4$ molecules. A comparison of the different physical properties of ionic compounds and covalent molecular substances is given in Table 2.1.3.

Table 2.1.3 The Physical Properties of Typical Ionic Compounds and Covalent Molecular Substances

| Ionic Compounds | Covalent Molecular Substances |
|---|---|
| hard solids | gases, liquids, or soft solids |
| high melting points | low melting points |
| nonvolatile | volatile |

Figure 2.1.8 *Interactions in Ionic and Covalent Solids*




*(a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane ($CH_4$) molecules in solid methane, a prototypical molecular solid, the methane molecules are held together in the solid only by relatively weak intermolecular forces, even though the atoms within each methane molecule are held together by strong covalent bonds.*

## Summary

The atoms in chemical compounds are held together by attractive electrostatic interactions known as **chemical bonds**. **Ionic compounds** contain positively and negatively charged ions in a ratio that results in an overall charge of zero. The ions are held together in a regular spatial arrangement by electrostatic forces. Most **covalent compounds** consist of **molecules**, groups of atoms in which one or more pairs of electrons are shared by at least two atoms to form a covalent bond. The atoms in molecules are held together by the **electrostatic attraction** between the positively charged nuclei of the bonded atoms and the negatively charged electrons shared by the nuclei. The **molecular formula** of a covalent compound gives the types and numbers of atoms present. Compounds that contain predominantly carbon and hydrogen are called **organic compounds**, whereas compounds that consist primarily of elements other than carbon and hydrogen are **inorganic compounds**. *Diatomic molecules* contain two atoms, and *polyatomic molecules* contain more than two. A **structural formula** indicates the composition and approximate structure and shape of a molecule. **Single bonds, double bonds**, and **triple bonds** are covalent bonds in which one, two, and three pairs of electrons, respectively, are shared between two bonded atoms. Atoms or groups of atoms that possess a net electrical charge are called *ions*; they can have either a positive charge (**cations**) or a negative charge (**anions**). Ions can consist of one atom (**monatomic ions**) or several (*polyatomic ions*). The charges on monatomic ions of most main group elements can be predicted from the location of the element in the periodic table. Ionic compounds usually form hard crystalline solids with high melting points. Covalent molecular compounds, in contrast, consist of discrete molecules held together by weak intermolecular forces and can be gases, liquids, or solids at room temperature and pressure.

## KEY TAKEAWAY

- There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties.

## CONCEPTUAL PROBLEMS

1. Ionic and covalent compounds are held together by electrostatic attractions between oppositely charged particles. Describe the differences in the nature of the attractions in ionic and covalent compounds. Which class of compounds contains pairs of

electrons shared between bonded atoms?

2. Which contains fewer electrons than the neutral atom—the corresponding cation or the anion?
3. What is the difference between an organic compound and an inorganic compound?
4. What is the advantage of writing a structural formula as a condensed formula?
5. The majority of elements that exist as diatomic molecules are found in one group of the periodic table. Identify the group.
6. Discuss the differences between covalent and ionic compounds with regard to
    1. the forces that hold the atoms together.
    2. melting points.
    3. physical states at room temperature and pressure.
7. Why do covalent compounds generally tend to have lower melting points than ionic compounds?

### Answer

1.
2.
3.
4.
5.
6.
7. Covalent compounds generally melt at lower temperatures than ionic compounds because the intermolecular interactions that hold the molecules together in a molecular solid are weaker than the electrostatic attractions that hold oppositely charged ions together in an ionic solid.

### NUMERICAL PROBLEMS

1. The structural formula for chloroform ($CHCl_3$) was shown in Example 2. Based on this information, draw the structural formula of dichloromethane ($CH_2Cl_2$).
2. What is the total number of electrons present in each ion?
    1. $F^-$
    2. $Rb^+$
    3. $Ce^{3+}$
    4. $Zr^{4+}$
    5. $Zn^{2+}$
    6. $Kr^{2+}$
    7. $B^{3+}$
3. What is the total number of electrons present in each ion?
    1. $Ca^{2+}$
    2. $Se^{2-}$
    3. $In^{3+}$
    4. $Sr^{2+}$
    5. $As^{3+}$
    6. $N^{3-}$
    7. $Tl^+$
4. Predict how many electrons are in each ion.
    1. an oxygen ion with a −2 charge
    2. a beryllium ion with a +2 charge
    3. a silver ion with a +1 charge
    4. a selenium ion with a +4 charge
    5. an iron ion with a +2 charge
    6. a chlorine ion with a −1 charge
5. Predict how many electrons are in each ion.

1. a copper ion with a +2 charge
2. a molybdenum ion with a +4 charge
3. an iodine ion with a −1 charge
4. a gallium ion with a +3 charge
5. an ytterbium ion with a +3 charge
6. a scandium ion with a +3 charge

6. Predict the charge on the most common monatomic ion formed by each element.
    1. chlorine
    2. phosphorus
    3. scandium
    4. magnesium
    5. arsenic
    6. oxygen
7. Predict the charge on the most common monatomic ion formed by each element.
    1. sodium
    2. selenium
    3. barium
    4. rubidium
    5. nitrogen
    6. aluminum
8. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
    1. X492+
    2. X11–
    3. X 8162–
9. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
    1. X37+
    2. X 919–
    3. X13273+

## AnswerS

1.
2.
3.
4.
5. 1. 27
    2. 38
    3. 54
    4. 28
    5. 67
    6. 18
6.
7.
8.
9. 1. Li, $Li^+$, 2nd period, group 1
    2. F, $F^–$, 2nd period, group 17
    3. Al, $Al^{3+}$, 3nd period, group 13

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# 2.2: Chemical Formulas

**Learning Objectives**

- To describe the composition of a chemical compound.

When chemists synthesize a new compound, they may not yet know its molecular or structural formula. In such cases, they usually begin by determining its **empirical formula**, the *relative* numbers of atoms of the elements in a compound, reduced to the smallest whole numbers. Because the empirical formula is based on experimental measurements of the numbers of atoms in a sample of the compound, it shows only the ratios of the numbers of the elements present. The difference between *empirical* and *molecular* formulas can be illustrated with butane, a covalent compound used as the fuel in disposable lighters. The molecular formula for butane is $C_4H_{10}$. The ratio of carbon atoms to hydrogen atoms in butane is 4:10, which can be reduced to 2:5. The empirical formula for butane is therefore $C_2H_5$. The **formula unit** is the *absolute* grouping of atoms or ions represented by the empirical formula of a compound, either ionic or covalent. Butane, for example, has the empirical formula $C_2H_5$, but it contains two $C_2H_5$ formula units, giving a molecular formula of $C_4H_{10}$.

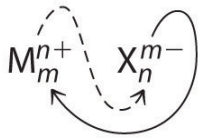
Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation and the anion have charges of equal magnitude, such as $Na^+$ and $Cl^-$, then the compound must have a 1:1 ratio of cations to anions, and the empirical formula must be NaCl. If the charges are not the same magnitude, then a cation:anion ratio other than 1:1 is needed to produce a neutral compound. In the case of $Mg^{2+}$ and $Cl^-$, for example, two $Cl^-$ ions are needed to balance the two positive charges on each $Mg^{2+}$ ion, giving an empirical formula of $MgCl_2$. Similarly, the formula for the ionic compound that contains $Na^+$ and $O^{2-}$ ions is $Na_2O$.

### Note the Pattern

Ionic compounds do not contain discrete molecules, so empirical formulas are used to indicate their compositions.

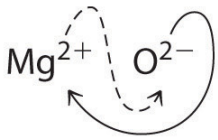
## Binary Ionic Compounds

An ionic compound that contains only two elements, one present as a cation and one as an anion, is called a **binary ionic compound**. One example is $MgCl_2$, a coagulant used in the preparation of tofu from soybeans. For binary ionic compounds, the subscripts in the empirical formula can also be obtained by crossing charges: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically as follows:




***Crossing charges.*** *One method for obtaining subscripts in the empirical formula is by crossing charges.*

When crossing charges, you will sometimes find it necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by $Mg^{2+}$ and $O^{2-}$. Using the absolute values of the charges on the ions as subscripts gives the formula $Mg_2O_2$:




This simplifies to its correct empirical formula MgO. The empirical formula has one $Mg^{2+}$ ion and one $O^{2-}$ ion.

## Example 2.2.1

1. $Ga^{3+}$ and $As^{3-}$
2. $Eu^{3+}$ and $O^{2-}$
3. calcium and chlorine

**Given:** ions or elements

**Asked for:** empirical formula for binary ionic compound

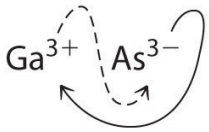
**Strategy:**

**A** If not given, determine the ionic charges based on the location of the elements in the periodic table.

**B** Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the lowest numbers to write the empirical formula. Check to make sure the empirical formula is electrically neutral.

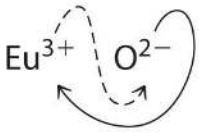
**Solution**

1. **B** Using the absolute values of the charges on the ions as the subscripts gives $Ga_3As_3$:




Reducing the subscripts to the smallest whole numbers gives the empirical formula GaAs, which is electrically neutral [+3 + (−3) = 0]. Alternatively, we could recognize that $Ga^{3+}$ and $As^{3-}$ have charges of equal magnitude but opposite signs. One $Ga^{3+}$ ion balances the charge on one $As^{3-}$ ion, and a 1:1 compound will have no net charge. Because we write subscripts only if the number is greater than 1, the empirical formula is GaAs. GaAs is gallium arsenide, which is widely used in the electronics industry in transistors and other devices.

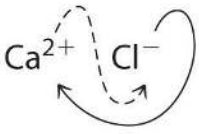
2. **B** Because $Eu^{3+}$ has a charge of +3 and $O^{2-}$ has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:




The subscript for $Eu^{3+}$ is 2 (from $O^{2-}$), and the subscript for $O^{2-}$ is 3 (from $Eu^{3+}$), giving $Eu_2O_3$; the subscripts cannot be reduced further. The empirical formula contains a positive charge of 2(+3) = +6 and a negative charge of 3(−2) = −6, for a net charge of 0. The compound $Eu_2O_3$ is neutral. Europium oxide is responsible for the red color in television and computer screens.

3. **A** Because the charges on the ions are not given, we must first determine the charges expected for the most common ions derived from calcium and chlorine. Calcium lies in group 2, so it should lose two electrons to form $Ca^{2+}$. Chlorine lies in group 17, so it should gain one electron to form $Cl^-$.

**B** Two $Cl^-$ ions are needed to balance the charge on one $Ca^{2+}$ ion, which leads to the empirical formula $CaCl_2$. We could also cross charges, using the absolute value of the charge on $Ca^{2+}$ as the subscript for Cl and the absolute value of the charge on $Cl^-$ as the subscript for Ca:



The subscripts in $CaCl_2$ cannot be reduced further. The empirical formula is electrically neutral [+2 + 2(−1) = 0]. This compound is calcium chloride, one of the substances used as “salt” to melt ice on roads and sidewalks in winter.

**? Exercise 2.2.1**

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

1. $Li^+$ and $N^{3-}$
2. $Al^{3+}$ and $O^{2-}$
3. lithium and oxygen

**Answer**

1. $Li_3N$
2. $Al_2O_3$
3. $Li_2O$

## Polyatomic Ions

**Polyatomic ions** are groups of atoms that bear a net electrical charge, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Two examples of polyatomic cations are the ammonium ($NH_4^+$) and the methylammonium ($CH_3NH_3^+$) ions. Polyatomic anions are much more numerous than polyatomic cations; some common examples are in Table 2.2.1.

Table 2.2.1 Common Polyatomic Ions and Their Names

| Formula | Name of Ion |
|---|---|
| $NH_4^+$ | ammonium |
| $CH_3NH_3^+$ | methylammonium |
| $OH^-$ | hydroxide |
| $O_2^{2-}$ | peroxide |
| $CN^-$ | cyanide |
| $SCN^-$ | thiocyanate |
| $NO_2^-$ | nitrite |
| $NO_3^-$ | nitrate |
| $CO_3^{2-}$ | carbonate |
| $HCO_3^-$ | hydrogen carbonate, or bicarbonate |
| $SO_3^{2-}$ | sulfite |
| $SO_4^{2-}$ | sulfate |
| $HSO_4^-$ | hydrogen sulfate, or bisulfate |
| $PO_4^{3-}$ | phosphate |
| $HPO_4^{2-}$ | hydrogen phosphate |
| $H_2PO_4^-$ | dihydrogen phosphate |
| $ClO^-$ | hypochlorite |
| $ClO_2^-$ | chlorite |
| $ClO_3^-$ | chlorate |
| $ClO_4^-$ | perchlorate |
| $MnO_4^-$ | permanganate |
| $CrO_4^{2-}$ | chromate |
| $Cr_2O_7^{2-}$ | dichromate |
| $C_2O_4^{2-}$ | oxalate |
| $HCO_2^-$ | formate |
| $CH_3CO_2^-$ | acetate |
| $C_6H_5CO_2^-$ | benzoate |

The method we used to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus $K^+$ and $NO_3^-$ ions combine in a 1:1 ratio to form $KNO_3$ (potassium nitrate or saltpeter), a major ingredient in black gunpowder. Similarly, $Ca^{2+}$ and $SO_4^{2-}$ form $CaSO_4$ (calcium sulfate), which combines with varying amounts of water to form gypsum and plaster of Paris. The polyatomic ions $NH_4^+$ and $NO_3^-$ form $NH_4NO_3$ (ammonium nitrate), which is a widely used fertilizer and, in the wrong hands, an explosive. One example of a compound in which the ions have charges of different magnitudes is calcium phosphate, which is composed of $Ca^{2+}$ and $PO_4^{3-}$ ions; it is a major component of bones. The compound is electrically neutral because the ions combine in a ratio of three $Ca^{2+}$ ions [3(+2) = +6] for every two ions [2(−3) = −6], giving an

empirical formula of $Ca_3(PO_4)_2$; the parentheses around $PO_4$ in the empirical formula indicate that it is a polyatomic ion. Writing the formula for calcium phosphate as $Ca_3P_2O_8$ gives the correct number of each atom in the formula unit, but it obscures the fact that the compound contains readily identifiable $PO_4^{3-}$ ions.

### Example 2.2.1

Write the empirical formula for the compound formed from each ion pair.

1. $Na^+$ and $HPO_4^{2-}$
2. potassium cation and cyanide anion
3. calcium cation and hypochlorite anion

**Given:** ions

**Asked for:** empirical formula for ionic compound

**Strategy:**

**A** If it is not given, determine the charge on a monatomic ion from its location in the periodic table. Use Table 2.4 to find the charge on a polyatomic ion.

**B** Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the smallest whole numbers when writing the empirical formula.

**Solution**

1. **B** Because $HPO_4^{2-}$ has a charge of −2 and $Na^+$ has a charge of +1, the empirical formula requires two $Na^+$ ions to balance the charge of the polyatomic ion, giving $Na_2HPO_4$. The subscripts are reduced to the lowest numbers, so the empirical formula is $Na_2HPO_4$. This compound is sodium hydrogen phosphate, which is used to provide texture in processed cheese, puddings, and instant breakfasts.
2. **A** The potassium cation is $K^+$, and the cyanide anion is $CN^-$. **B** Because the magnitude of the charge on each ion is the same, the empirical formula is KCN. Potassium cyanide is highly toxic, and at one time it was used as rat poison. This use has been discontinued, however, because too many people were being poisoned accidentally.
3. **A** The calcium cation is $Ca^{2+}$, and the hypochlorite anion is $ClO^-$. **B** Two $ClO^-$ ions are needed to balance the charge on one $Ca^{2+}$ ion, giving $Ca(ClO)_2$. The subscripts cannot be reduced further, so the empirical formula is $Ca(ClO)_2$. This is calcium hypochlorite, the “chlorine” used to purify water in swimming pools.

### Exercise 2.2.1

Write the empirical formula for the compound formed from each ion pair.

1. $Ca^{2+}$ and $H_2PO_4^-$
2. sodium cation and bicarbonate anion
3. ammonium cation and sulfate anion

1. $Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.
2. $NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.
3. $(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

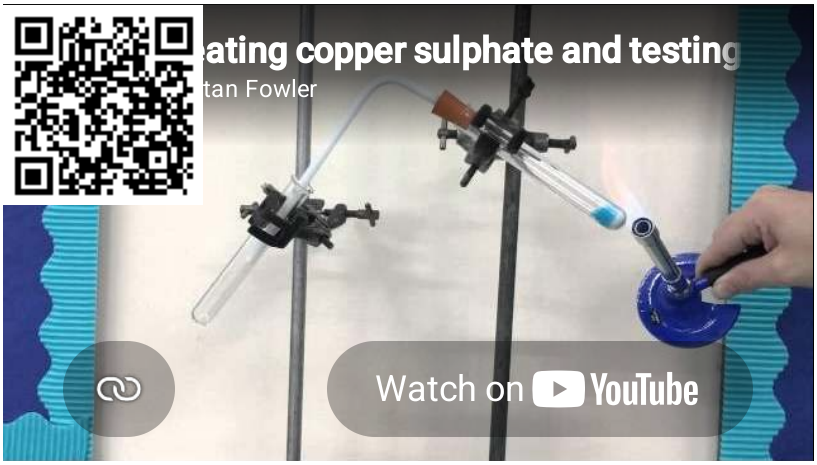
**Answer**

## Hydrates

Many ionic compounds occur as **hydrates**, compounds that contain specific ratios of loosely bound water molecules, called **waters of hydration**. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate can form a solid that contains one molecule of water per $Ca(H_2PO_4)_2$ unit and is used as a leavening agent in the food industry to cause baked goods to rise. The empirical formula for the solid is $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, copper sulfate usually forms a blue solid

that contains *five* waters of hydration per formula unit, with the empirical formula $CuSO_4 \cdot 5H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$ (Figure 2.9).

*Loss of Water from a Hydrate with Heating*




*When blue $CuSO_4 \cdot 5H_2O$ is heated, two molecules of water are lost at 30°C, two more at 110°C, and the last at 250°C to give white $CuSO_4$.*

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $CaSO_4 \cdot \frac{1}{2}H_2O$ is plaster of Paris, which was often used to make sturdy casts for broken arms or legs, whereas $CaSO_4 \cdot 2H_2O$ is the less dense, flakier gypsum, a mineral used in drywall panels for home construction. When a cast would set, a mixture of plaster of Paris and water crystallized to give solid $CaSO_4 \cdot 2H_2O$. Similar processes are used in the setting of cement and concrete.

## Summary

An **empirical formula** gives the *relative* numbers of atoms of the elements in a compound, reduced to the lowest whole numbers. The **formula unit** is the *absolute* grouping represented by the empirical formula of a compound, either ionic or covalent. Empirical formulas are particularly useful for describing the composition of ionic compounds, which do not contain readily identifiable molecules. Some ionic compounds occur as **hydrates**, which contain specific ratios of loosely bound water molecules called **waters of hydration**.

## KEY TAKEAWAY

- The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit.

## CONCEPTUAL PROBLEMS

1. What are the differences and similarities between a polyatomic ion and a molecule?
2. Classify each compound as ionic or covalent.
    1. $Zn_3(PO_4)_2$
    2. $C_6H_5CO_2H$
    3. $K_2Cr_2O_7$
    4. $CH_3CH_2SH$
    5. $NH_4Br$
    6. $CCl_2F_2$
3. Classify each compound as ionic or covalent. Which are organic compounds and which are inorganic compounds?
    1. $CH_3CH_2CO_2H$
    2. $CaCl_2$
    3. $Y(NO_3)_3$
    4. $H_2S$
    5. $NaC_2H_3O_2$

4. Generally, one cannot determine the molecular formula directly from an empirical formula. What other information is needed?
5. Give two pieces of information that we obtain from a structural formula that we cannot obtain from an empirical formula.
6. The formulas of alcohols are often written as ROH rather than as empirical formulas. For example, methanol is generally written as $CH_3OH$ rather than $CH_4O$. Explain why the ROH notation is preferred.
7. The compound dimethyl sulfide has the empirical formula $C_2H_6S$ and the structural formula $CH_3SCH_3$. What information do we obtain from the structural formula that we do not get from the empirical formula? Write the condensed structural formula for the compound.
8. What is the correct formula for magnesium hydroxide—$MgOH_2$ or $Mg(OH)_2$? Why?
9. Magnesium cyanide is written as $Mg(CN)_2$, not $MgCN_2$. Why?
10. Does a given hydrate always contain the same number of waters of hydration?

## Answer

1.
2.
3.
4.
5.
6.
7. The structural formula gives us the connectivity of the atoms in the molecule or ion, as well as a schematic representation of their arrangement in space. Empirical formulas tell us only the ratios of the atoms present. The condensed structural formula of dimethylsulfide is $(CH_3)_2S$.
8.
9.
10.

## NUMERICAL PROBLEMS

1. Write the formula for each compound.
    1. magnesium sulfate, which has 1 magnesium atom, 4 oxygen atoms, and 1 sulfur atom
    2. ethylene glycol (antifreeze), which has 6 hydrogen atoms, 2 carbon atoms, and 2 oxygen atoms
    3. acetic acid, which has 2 oxygen atoms, 2 carbon atoms, and 4 hydrogen atoms
    4. potassium chlorate, which has 1 chlorine atom, 1 potassium atom, and 3 oxygen atoms
    5. sodium hypochlorite pentahydrate, which has 1 chlorine atom, 1 sodium atom, 6 oxygen atoms, and 10 hydrogen atoms
2. Write the formula for each compound.
    1. cadmium acetate, which has 1 cadmium atom, 4 oxygen atoms, 4 carbon atoms, and 6 hydrogen atoms
    2. barium cyanide, which has 1 barium atom, 2 carbon atoms, and 2 nitrogen atoms
    3. iron(III) phosphate dihydrate, which has 1 iron atom, 1 phosphorus atom, 6 oxygen atoms, and 4 hydrogen atoms
    4. manganese(II) nitrate hexahydrate, which has 1 manganese atom, 12 hydrogen atoms, 12 oxygen atoms, and 2 nitrogen atoms
    5. silver phosphate, which has 1 phosphorus atom, 3 silver atoms, and 4 oxygen atoms
3. Complete the following table by filling in the formula for the ionic compound formed by each cation-anion pair.

| Ion | $K^+$ | $Fe^{3+}$ | $NH_4^+$ | $Ba^{2+}$ |
|---|---|---|---|---|
| $Cl^-$ | KCl | | | |
| $SO_4^{2-}$ | | | | |
| $PO_4^{3-}$ | | | | |
| $NO_3^-$ | | | | |
| $OH^-$ | | | | |

4. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
    1. zinc and sulfur
    2. barium and iodine
    3. magnesium and chlorine
    4. silicon and oxygen
    5. sodium and sulfur
5. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
    1. lithium and nitrogen
    2. cesium and chlorine
    3. germanium and oxygen
    4. rubidium and sulfur
    5. arsenic and sodium
6. Write the empirical formula for each compound.
    1. $Na_2S_2O_4$
    2. $B_2H_6$
    3. $C_6H_{12}O_6$
    4. $P_4O_{10}$
    5. $KMnO_4$
7. Write the empirical formula for each compound.
    1. $Al_2Cl_6$
    2. $K_2Cr_2O_7$
    3. $C_2H_4$
    4. $(NH_2)_2CNH$
    5. $CH_3COOH$

## AnswerS

1. 1. $MgSO_4$
    2. $C_2H_6O_2$
    3. $C_2H_4O_2$
    4. $KClO_3$
    5. $NaOCl·5H_2O$
2. 
3. 

| Ion | **K** $^{+}$ | **Fe** $^{3+}$ | **NH** $_4$ $^{+}$ | **Ba** $^{2+}$ |
|---|---|---|---|---|
| **Cl** $^{-}$ | **KCl** | $FeCl_3$ | $NH_4Cl$ | $BaCl_2$ |
| **SO** $_4$ $^{2-}$ | $K_2SO_4$ | $Fe_2(SO_4)_3$ | $(NH_4)_2SO_4$ | $BaSO_4$ |
| **PO** $_4$ $^{3-}$ | $K_3PO_4$ | $FePO_4$ | $(NH_4)_3PO_4$ | $Ba_3(PO_4)_2$ |
| **NO** $_3$ $^{-}$ | $KNO_3$ | $Fe(NO_3)_3$ | $NH_4NO_3$ | $Ba(NO_3)_2$ |
| **OH** $^{-}$ | KOH | $Fe(OH)_3$ | $NH_4OH$ | $Ba(OH)_2$ |

4. 
5. 1. $Li_3N$
    2. CsCl
    3. $GeO_2$
    4. $Rb_2S$

5. $Na_3As$

6.

7. 1. $AlCl_3$
   2. $K_2Cr_2O_7$
   3. $CH_2$
   4. $CH_5N_3$
   5. $CH_2O$

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# 2.3: Naming Ionic Compounds

**Learning Objectives**

- To name ionic compounds.

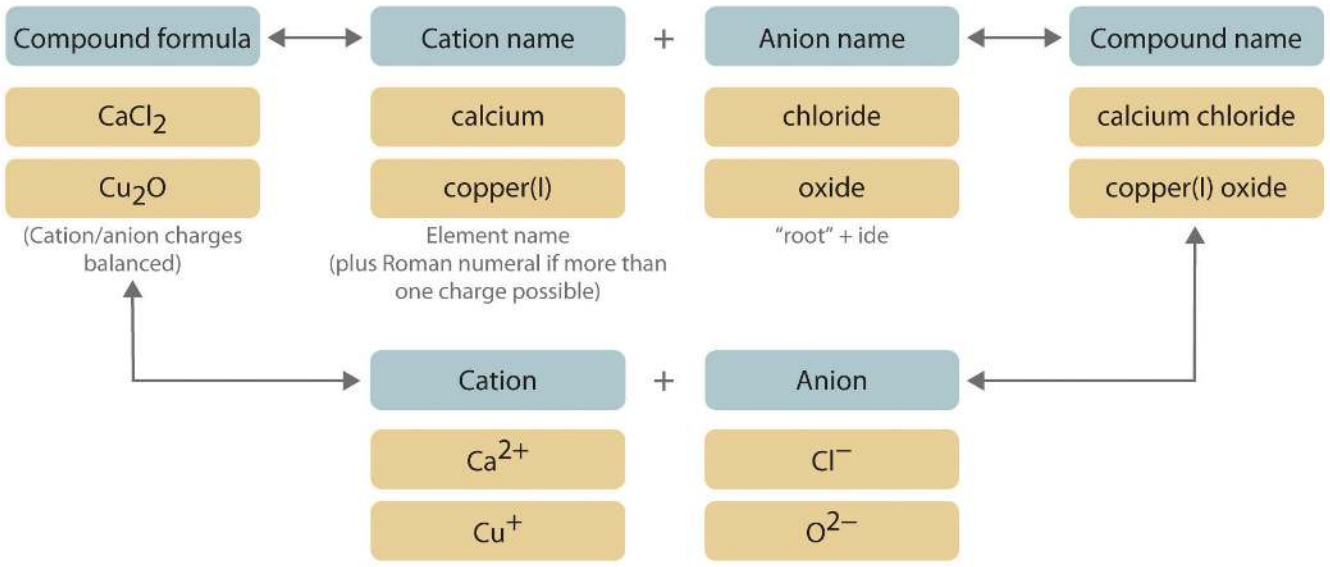
The empirical and molecular formulas discussed in the preceding section are precise and highly informative, but they have some disadvantages. First, they are inconvenient for routine verbal communication. For example, saying "C-A-three-P-O-four-two" for $Ca_3(PO_4)_2$ is much more difficult than saying "calcium phosphate." In addition, you will see in Section 2.4 that many compounds have the same empirical and molecular formulas but different arrangements of atoms, which result in very different chemical and physical properties. In such cases, it is necessary for the compounds to have different names that distinguish among the possible arrangements.

Many compounds, particularly those that have been known for a relatively long time, have more than one name: a *common* name (sometimes more than one) and a *systematic* name, which is the name assigned by adhering to specific rules. Like the names of most elements, the common names of chemical compounds generally have historical origins, although they often appear to be unrelated to the compounds of interest. For example, the systematic name for $KNO_3$ is potassium nitrate, but its common name is saltpeter.

In this text, we use a systematic nomenclature to assign meaningful names to the millions of known substances. Unfortunately, some chemicals that are widely used in commerce and industry are still known almost exclusively by their common names; in such cases, you must be familiar with the common name as well as the systematic one. The objective of this and the next two sections is to teach you to write the formula for a simple inorganic compound from its name—and vice versa—and introduce you to some of the more frequently encountered common names.

We begin with *binary ionic compounds*, which contain only two elements. The procedure for naming such compounds is outlined in Figure 2.3.1 and uses the following steps:

Figure 2.3.1 *Naming an Ionic Compound*




1. Place the ions in their proper order: cation and then anion.
2. Name the cation.
    1. **Metals that form only one cation.** As noted in Section 2.1, these metals are usually in groups 1–3, 12, and 13. The name of the cation of a metal that forms only one cation is the same as the name of the metal (with the word *ion* added if the cation is by itself). For example, $Na^+$ is the sodium ion, $Ca^{2+}$ is the calcium ion, and $Al^{3+}$ is the aluminum ion.

2. **Metals that form more than one cation.** As shown in Figure 2.3.2, many metals can form more than one cation. This behavior is observed for most transition metals, many actinides, and the heaviest elements of groups 13–15. In such cases, the positive charge on the metal is indicated by a roman numeral in parentheses immediately following the name of the metal. Thus $Cu^{+}$ is copper(I) (read as "copper one"), $Fe^{2+}$ is iron(II), $Fe^{3+}$ is iron(III), $Sn^{2+}$ is tin(II), and $Sn^{4+}$ is tin(IV).

   An older system of nomenclature for such cations is still widely used, however. The name of the cation with the *higher* charge is formed from the root of the element's Latin name with the suffix *-ic* attached, and the name of the cation with the *lower* charge has the same root with the suffix *-ous*. The names of $Fe^{3+}$, $Fe^{2+}$, $Sn^{4+}$, and $Sn^{2+}$ are therefore ferric, ferrous, stannic, and stannous, respectively. Even though this text uses the systematic names with roman numerals, you should be able to recognize these common names because they are still often used. For example, on the label of your dentist's fluoride rinse, the compound chemists call tin(II) fluoride is usually listed as stannous fluoride.

   Some examples of metals that form more than one cation are in Table 2.3.1 along with the names of the ions. Note that the simple $Hg^{+}$ cation does not occur in chemical compounds. Instead, all compounds of mercury(I) contain a *dimeric* cation, $Hg_2^{2+}$, in which the two Hg atoms are bonded together.

   Table 2.3.1 Common Cations of Metals That Form More Than One Ion

| Cation | Systematic Name | Common Name | Cation | Systematic Name | Common Name |
|---|---|---|---|---|---|
| $Cr^{2+}$ | chromium(II) | chromous | $Cu^{2+}$ | copper(II) | cupric |
| $Cr^{3+}$ | chromium(III) | chromic | $Cu^{+}$ | copper(I) | cuprous |
| $Mn^{2+}$ | manganese(II) | manganous* | $Hg^{2+}$ | mercury(II) | mercuric |
| $Mn^{3+}$ | manganese(III) | manganic* | $Hg_2^{2+}$ | mercury(I) | mercurous† |
| $Fe^{2+}$ | iron(II) | ferrous | $Sn^{4+}$ | tin(IV) | stannic |
| $Fe^{3+}$ | iron(III) | ferric | $Sn^{2+}$ | tin(II) | stannous |
| $Co^{2+}$ | cobalt(II) | cobaltous* | $Pb^{4+}$ | lead(IV) | plumbic* |
| $Co^{3+}$ | cobalt(III) | cobaltic* | $Pb^{2+}$ | lead(II) | plumbous* |

   * Not widely used.

   †The isolated mercury(I) ion exists only as the gaseous ion.

3. **Polyatomic cations.** The names of the common polyatomic cations that are relatively important in ionic compounds (such as, the ammonium ion) are in Table 2.4.

3. Name the anion.

1. **Monatomic anions.** Monatomic anions are named by adding the suffix *-ide* to the root of the name of the parent element; thus, $Cl^{-}$ is chloride, $O^{2-}$ is oxide, $P^{3-}$ is phosphide, $N^{3-}$ is nitride (also called azide), and $C^{4-}$ is carbide. Because the charges on these ions can be predicted from their position in the periodic table, it is *not* necessary to specify the charge in the name. Examples of monatomic anions are in
2. **Polyatomic anions.** Polyatomic anions typically have common names that you must learn; some examples are in Table 2.4. Polyatomic anions that contain a single metal or nonmetal atom plus one or more oxygen atoms are called *oxoanions (or oxyanions)*. In cases where only two oxoanions are known for an element, the name of the oxoanion with more oxygen atoms ends in *-ate*, and the name of the oxoanion with fewer oxygen atoms ends in *-ite*. For example, $NO_{3-}$ is nitrate and $NO_{2-}$ is nitrite.

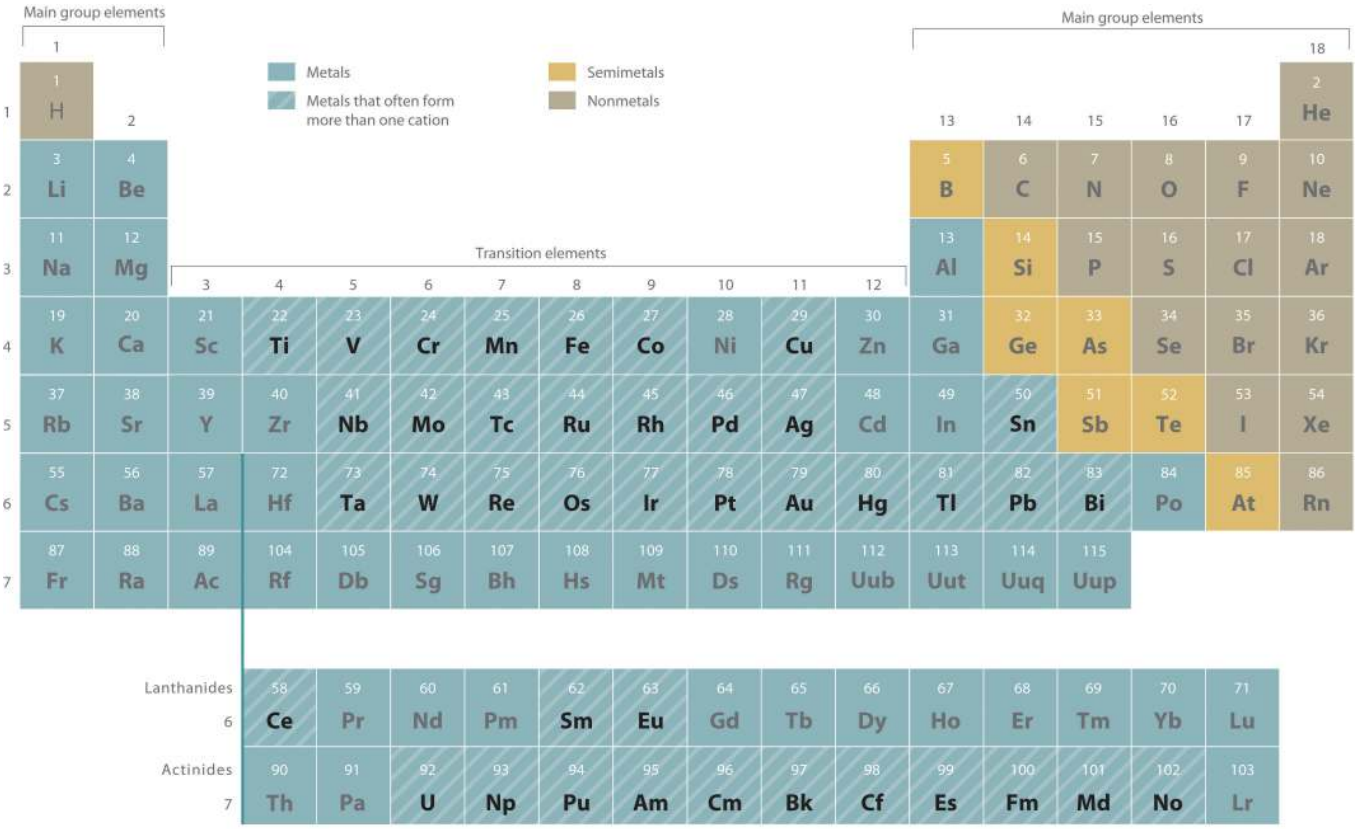
   The halogens and some of the transition metals form more extensive series of oxoanions with as many as four members. In the names of these oxoanions, the prefix *per-* is used to identify the oxoanion with the most oxygen (so that $ClO_4^{-}$ is perchlorate and $ClO_3^{-}$ is chlorate), and the prefix *hypo-* is used to identify the anion with the fewest oxygen ($ClO_2^{-}$ is chlorite and $ClO^{-}$ is hypochlorite). The relationship between the names of oxoanions and the number of oxygen atoms present is diagrammed in Figure 2.12. Differentiating the oxoanions in such a series is no trivial matter. For example, the

hypochlorite ion is the active ingredient in laundry bleach and swimming pool disinfectant, but compounds that contain the perchlorate ion can explode if they come into contact with organic substances.

4. Write the name of the compound as the name of the cation followed by the name of the anion.

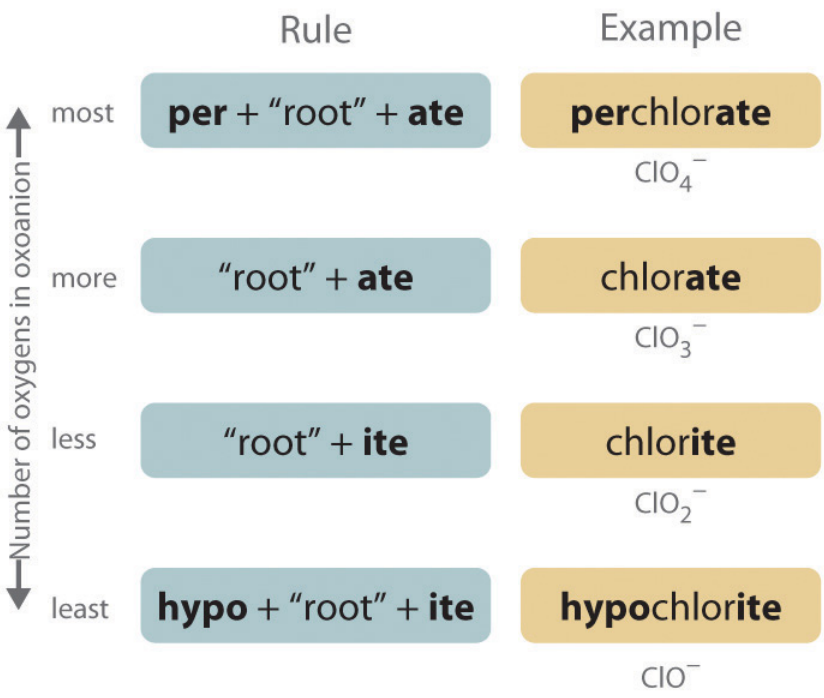
   It is *not* necessary to indicate the number of cations or anions present per formula unit in the name of an ionic compound because this information is implied by the charges on the ions. You must consider the charge of the ions when writing the formula for an ionic compound from its name, however. Because the charge on the chloride ion is −1 and the charge on the calcium ion is +2, for example, consistent with their positions in the periodic table, simple arithmetic tells you that calcium chloride must contain twice as many chloride ions as calcium ions to maintain electrical neutrality. Thus the formula is $CaCl_2$. Similarly, calcium phosphate must be $Ca_3(PO_4)_2$ because the cation and the anion have charges of +2 and −3, respectively. The best way to learn how to name ionic compounds is to work through a few examples, referring to Figure 2.10, Table 2.2, Table 2.4, and Table 2.5 as needed.

Figure 2.3.2 *Metals That Form More Than One Cation and Their Locations in the Periodic Table*




*With only a few exceptions, these metals are usually transition metals or actinides.*

Figure 2.3.3 *The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present*




## Note the Pattern

Cations are always named before anions.

Most transition metals, many actinides, and the heaviest elements of groups 13–15 can form more than one cation.

### Example 2.3.1

Write the systematic name (and the common name if applicable) for each ionic compound.

1. LiCl
2. $MgSO_4$
3. $(NH_4)_3PO_4$
4. $Cu_2O$

**Given:** empirical formula

**Asked for:** name

**Strategy:**

**A** If only one charge is possible for the cation, give its name, consulting Table 2.2 or Table 2.4 if necessary. If the cation can have more than one charge (Table 2.3.1), specify the charge using roman numerals.

**B** If the anion does not contain oxygen, name it according to step 3a, using Table 2.2 and Table 2.4 if necessary. For polyatomic anions that contain oxygen, use Table 2.4 and the appropriate prefix and suffix listed in step 3b.

**C** Beginning with the cation, write the name of the compound.

**Solution**

1. **A B** Lithium is in group 1, so we know that it forms only the $Li^+$ cation, which is the lithium ion. Similarly, chlorine is in group 7, so it forms the $Cl^-$ anion, which is the chloride ion. **C** Because we begin with the name of the cation, the name of this compound is lithium chloride, which is used medically as an antidepressant drug.
2. **A B** The cation is the magnesium ion, and the anion, which contains oxygen, is sulfate. **C** Because we list the cation first, the name of this compound is magnesium sulfate. A hydrated form of magnesium sulfate ($MgSO_4 \cdot 7H_2O$) is sold in drugstores as Epsom salts, a harsh but effective laxative.

3. **A B** The cation is the ammonium ion (from Table 2.4), and the anion is phosphate. **C** The compound is therefore ammonium phosphate, which is widely used as a fertilizer. It is not necessary to specify that the formula unit contains three ammonium ions because three are required to balance the negative charge on phosphate.
4. **A B** The cation is a transition metal that often forms more than one cation (Table 2.5). We must therefore specify the positive charge on the cation in the name: copper(I) or, according to the older system, cuprous. The anion is oxide. **C** The name of this compound is copper(I) oxide or, in the older system, cuprous oxide. Copper(I) oxide is used as a red glaze on ceramics and in antifouling paints to prevent organisms from growing on the bottoms of boats.

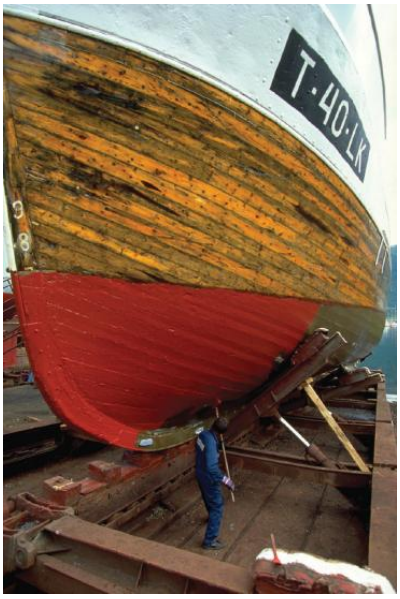
## ? Exercise 2.3.1

Write the systematic name (and the common name if applicable) for each ionic compound.\

1. $CuCl_2$
2. $MgCO_3$
3. $FePO_4$

**Answer**

1. copper(II) chloride (or cupric chloride)
2. magnesium carbonate
3. iron(III) phosphate (or ferric phosphate)




***$Cu_2O$.*** *The bottom of a boat is protected with a red antifouling paint containing copper(I) oxide, $Cu_2O$.*

## ✔ Example 2.3.1

Write the formula for each compound.

1. calcium dihydrogen phosphate
2. aluminum sulfate
3. chromium(III) oxide

**Given:** systematic name

**Asked for:** formula

**Strategy:**

**A** Identify the cation and its charge using the location of the element in the periodic table and Table 2.2, Table 2.3, Table 2.4, and Table 2.5. If the cation is derived from a metal that can form cations with different charges, use the appropriate roman numeral or suffix to indicate its charge.

**B** Identify the anion using Table 2.2 and Table 2.4. Beginning with the cation, write the compound's formula and then determine the number of cations and anions needed to achieve electrical neutrality.

**Solution**

1. **A** Calcium is in group 2, so it forms only the $Ca^{2+}$ ion. **B** Dihydrogen phosphate is the $H_2PO_4^-$ ion (Table 2.4). Two $H_2PO_4^-$ ions are needed to balance the positive charge on $Ca^{2+}$, to give $Ca(H_2PO_4)_2$. A hydrate of calcium dihydrogen phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, is the active ingredient in baking powder.
2. **A** Aluminum, near the top of group 13 in the periodic table, forms only one cation, $Al^{3+}$ (Figure 2.11). **B** Sulfate is $SO_4^{2-}$ (Table 2.4). To balance the electrical charges, we need two $Al^{3+}$ cations and three $SO_4^{2-}$ anions, giving $Al_2(SO_4)_3$. Aluminum sulfate is used to tan leather and purify drinking water.
3. **A** Because chromium is a transition metal, it can form cations with different charges. The roman numeral tells us that the positive charge in this case is +3, so the cation is $Cr^{3+}$. **B** Oxide is $O^{2-}$. Thus two cations ($Cr^{3+}$) and three anions ($O^{2-}$) are required to give an electrically neutral compound, $Cr_2O_3$. This compound is a common green pigment that has many uses, including camouflage coatings.




***$Cr_2O_3$.*** *Chromium(III) oxide ($Cr_2O_3$) is a common pigment in dark green paints, such as camouflage paint.*

**? Exercise 2.3.1**

Write the formula for each compound.

1. barium chloride

2. sodium carbonate
3. iron(III) hydroxide

**Answer**

1. $BaCl_2$
2. $Na_2CO_3$
3. $Fe(OH)_3$

## Summary

Ionic compounds are named according to systematic procedures, although common names are widely used. Systematic nomenclature enables us to write the structure of any compound from its name and vice versa. Ionic compounds are named by writing the cation first, followed by the anion. If a metal can form cations with more than one charge, the charge is indicated by roman numerals in parentheses following the name of the metal. **Oxoanions** are polyatomic anions that contain a single metal or nonmetal atom and one or more oxygen atoms.

## KEY TAKEAWAY

- There is a systematic method used to name ionic compounds.

## CONCEPTUAL PROBLEMS

1. Name each cation.
    1. $K^+$
    2. $Al^{3+}$
    3. $NH_4^+$
    4. $Mg^{2+}$
    5. $Li^+$
2. Name each anion.
    1. $Br^-$
    2. $CO_3^{2-}$
    3. $S^{2-}$
    4. $NO_3^-$
    5. $HCO_2^-$
    6. $F^-$
    7. $ClO^-$
    8. $C_2O_4^{2-}$
3. Name each anion.
    1. $PO_4^{3-}$
    2. $Cl^-$
    3. $SO_3^{2-}$
    4. $CH_3CO_2^-$
    5. $HSO_4^-$
    6. $ClO_4^-$
    7. $NO_2^-$
    8. $O^{2-}$
4. Name each anion.
    1. $SO_4^{2-}$
    2. $CN^-$
    3. $Cr_2O_7^{2-}$
    4. $N^{3-}$
    5. $OH^-$

6. $I^-$
7. $O_2^{2-}$

5. Name each compound.
   1. $MgBr_2$
   2. $NH_4CN$
   3. $CaO$
   4. $KClO_3$
   5. $K_3PO_4$
   6. $NH_4NO_2$
   7. $NaN_3$
6. Name each compound.
   1. $NaNO_3$
   2. $Cu_3(PO_4)_2$
   3. $NaOH$
   4. $Li_4C$
   5. $CaF_2$
   6. $NH_4Br$
   7. $MgCO_3$
7. Name each compound.
   1. $RbBr$
   2. $Mn_2(SO_4)_3$
   3. $NaClO$
   4. $(NH_4)_2SO_4$
   5. $NaBr$
   6. $KIO_3$
   7. $Na_2CrO_4$
8. Name each compound.
   1. $NH_4ClO_4$
   2. $SnCl_4$
   3. $Fe(OH)_2$
   4. $Na_2O$
   5. $MgCl_2$
   6. $K_2SO_4$
   7. $RaCl_2$
9. Name each compound.
   1. $KCN$
   2. $LiOH$
   3. $CaCl_2$
   4. $NiSO_4$
   5. $NH_4ClO_2$
   6. $LiClO_4$
   7. $La(CN)_3$

## Answer

1.
2.
3.
4.

5.
6.
7. 1. rubidium bromide
   2. manganese(III) sulfate
   3. sodium hypochlorite
   4. ammonium sulfate
   5. sodium bromide
   6. potassium iodate
   7. sodium chromate
8.
9.

## NUMERICAL PROBLEMS

1. For each ionic compound, name the cation and the anion and give the charge on each ion.
   1. BeO
   2. $Pb(OH)_2$
   3. BaS
   4. $Na_2Cr_2O_7$
   5. $ZnSO_4$
   6. KClO
   7. $NaH_2PO_4$
2. For each ionic compound, name the cation and the anion and give the charge on each ion.
   1. $Zn(NO_3)_2$
   2. CoS
   3. $BeCO_3$
   4. $Na_2SO_4$
   5. $K_2C_2O_4$
   6. NaCN
   7. $FeCl_2$
3. Write the formula for each compound.
   1. magnesium carbonate
   2. aluminum sulfate
   3. potassium phosphate
   4. lead(IV) oxide
   5. silicon nitride
   6. sodium hypochlorite
   7. titanium(IV) chloride
   8. disodium ammonium phosphate
4. Write the formula for each compound.
   1. lead(II) nitrate
   2. ammonium phosphate
   3. silver sulfide
   4. barium sulfate
   5. cesium iodide
   6. sodium bicarbonate
   7. potassium dichromate
   8. sodium hypochlorite
5. Write the formula for each compound.

1. zinc cyanide
2. silver chromate
3. lead(II) iodide
4. benzene
5. copper(II) perchlorate

6. Write the formula for each compound.
    1. calcium fluoride
    2. sodium nitrate
    3. iron(III) oxide
    4. copper(II) acetate
    5. sodium nitrite
7. Write the formula for each compound.
    1. sodium hydroxide
    2. calcium cyanide
    3. magnesium phosphate
    4. sodium sulfate
    5. nickel(II) bromide
    6. calcium chlorite
    7. titanium(IV) bromide
8. Write the formula for each compound.
    1. sodium chlorite
    2. potassium nitrite
    3. sodium nitride (also called sodium azide)
    4. calcium phosphide
    5. tin(II) chloride
    6. calcium hydrogen phosphate
    7. iron(II) chloride dihydrate
9. Write the formula for each compound.
    1. potassium carbonate
    2. chromium(III) sulfite
    3. cobalt(II) phosphate
    4. magnesium hypochlorite
    5. nickel(II) nitrate hexahydrate

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# 2.4: Naming Covalent Compounds

**Learning Objectives**

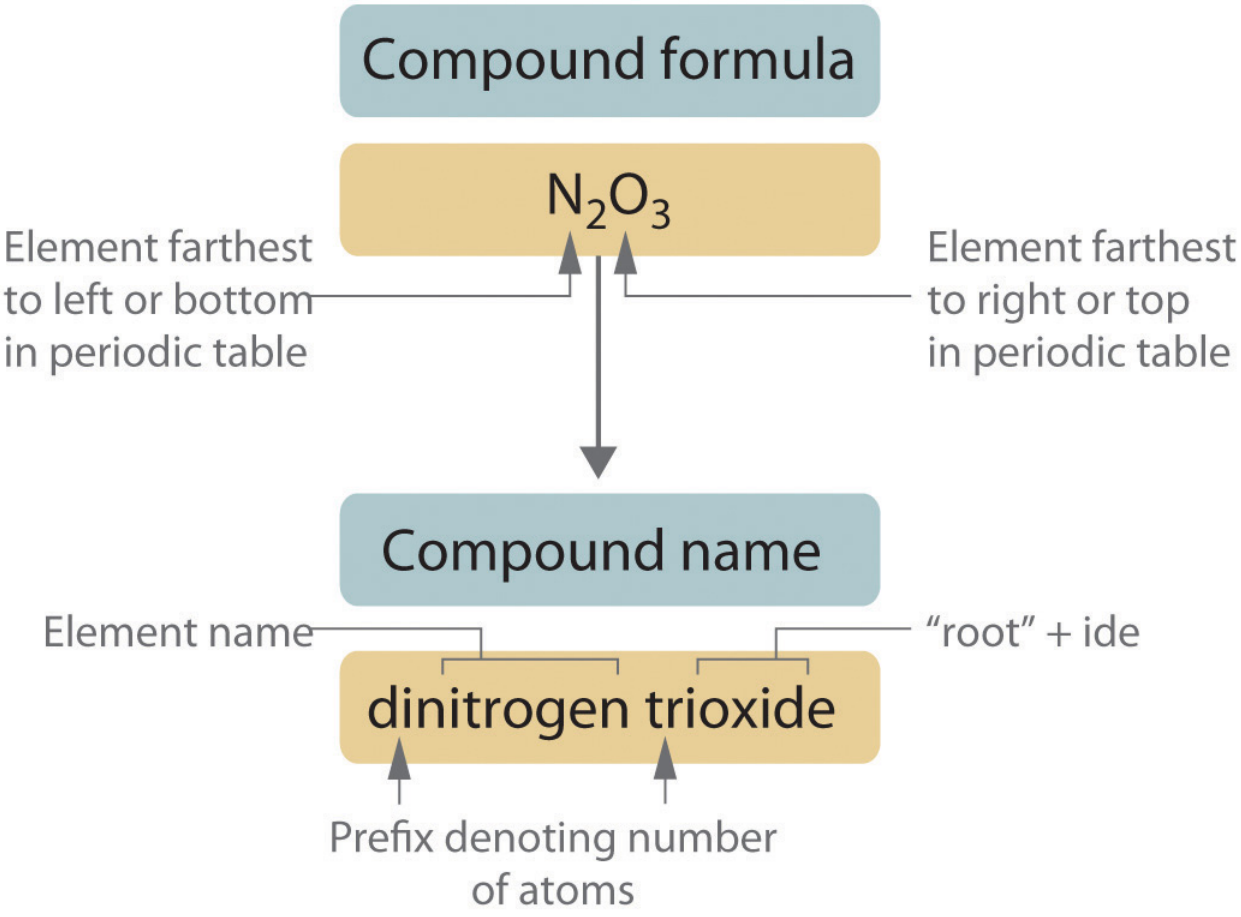
- To name covalent compounds that contain up to three elements.

As with ionic compounds, the system that chemists have devised for naming covalent compounds enables us to write the molecular formula from the name and vice versa. In this and the following section, we describe the rules for naming simple covalent compounds. We begin with inorganic compounds and then turn to simple organic compounds that contain only carbon and hydrogen.

## Binary Inorganic Compounds

*Binary covalent compounds*—that is, covalent compounds that contain only two elements—are named using a procedure similar to that used to name simple ionic compounds, but prefixes are added as needed to indicate the number of atoms of each kind. The procedure, diagrammed in Figure 2.4.1, uses the following steps:

Figure 2.4.1 *Naming a Covalent Inorganic Compound*




1. Place the elements in their proper order.
    1. The element farthest to the left in the periodic table is usually named first. If both elements are in the same group, the element closer to the bottom of the column is named first.
    2. The second element is named as if it were a monatomic anion in an ionic compound (even though it is not), with the suffix -*ide* attached to the root of the element name.
2. Identify the number of each type of atom present.

1. Prefixes derived from Greek stems are used to indicate the number of each type of atom in the formula unit (Table 2.4.1 ). The prefix *mono-* (“one”) is used only when absolutely necessary to avoid confusion, just as we omit the subscript 1 when writing molecular formulas.

   To demonstrate steps 1 and 2a, we name HCl as hydrogen chloride (because hydrogen is to the left of chlorine in the periodic table) and $PCl_5$ as phosphorus pentachloride. The order of the elements in the name of $BrF_3$, bromine trifluoride, is determined by the fact that bromine lies below fluorine in group 17.

   Table 2.4.1 Prefixes for Indicating the Number of Atoms in Chemical Names

| Prefix | Number |
|---|---|
| mono- | 1 |
| di- | 2 |
| tri- | 3 |
| tetra- | 4 |
| penta- | 5 |
| hexa- | 6 |
| hepta- | 7 |
| octa- | 8 |
| nona- | 9 |
| deca- | 10 |
| undeca- | 11 |
| dodeca- | 12 |

2. If a molecule contains more than one atom of both elements, then prefixes are used for both. Thus $N_2O_3$ is *di*nitrogen *tri*oxide, as shown in Figure 2.4.1.
3. In some names, the final *a* or *o* of the prefix is dropped to avoid awkward pronunciation. Thus $OsO_4$ is osmium tetroxide rather than osmium tetraoxide.

3. Write the name of the compound.
   1. Binary compounds of the elements with oxygen are generally named as “element oxide,” with prefixes that indicate the number of atoms of each element per formula unit. For example, CO is carbon monoxide. The only exception is binary compounds of oxygen with fluorine, which are named as oxygen fluorides. (The reasons for this convention will become clear in Chapter 7 and Chapter 8.)
   2. Certain compounds are *always* called by the common names that were assigned long ago when names rather than formulas were used. For example, $H_2O$ is water (not dihydrogen oxide); $NH_3$ is ammonia; $PH_3$ is phosphine; $SiH_4$ is silane; and $B_2H_6$, a *dimer* of $BH_3$, is diborane. For many compounds, the systematic name and the common name are both used frequently, so you must be familiar with them. For example, the systematic name for NO is nitrogen monoxide, but it is much more commonly called nitric oxide. Similarly, $N_2O$ is usually called nitrous oxide rather than dinitrogen monoxide. Notice that the suffixes *-ic* and *-ous* are the same ones used for ionic compounds.

### Note the Pattern

Start with the element at the far left in the periodic table and work to the right. If two or more elements are in the same group, start with the bottom element and work up.

## Example 2.4.1

Write the name of each binary covalent compound.

1. $SF_6$
2. $N_2O_4$
3. $ClO_2$

**Given:** molecular formula

**Asked for:** name of compound

**Strategy:**

**A** List the elements in order according to their positions in the periodic table. Identify the number of each type of atom in the chemical formula and then use Table 2.4.1 to determine the prefixes needed.

**B** If the compound contains oxygen, follow step 3a. If not, decide whether to use the common name or the systematic name.

**Solution**

1. **A** Because sulfur is to the left of fluorine in the periodic table, sulfur is named first. Because there is only one sulfur atom in the formula, no prefix is needed. **B** There are, however, six fluorine atoms, so we use the prefix for six: *hexa-* (Table 2.4.1). The compound is sulfur hexafluoride.
2. **A** Because nitrogen is to the left of oxygen in the periodic table, nitrogen is named first. Because more than one atom of each element is present, prefixes are needed to indicate the number of atoms of each. According to Table 2.4.1, the prefix for two is *di-*, and the prefix for four is *tetra-*. **B** The compound is dinitrogen tetroxide (omitting the *a* in *tetra-* according to step 2c) and is used as a component of some rocket fuels.
3. **A** Although oxygen lies to the left of chlorine in the periodic table, it is not named first because $ClO_2$ is an oxide of an element other than fluorine (step 3a). Consequently, chlorine is named first, but a prefix is not necessary because each molecule has only one atom of chlorine. **B** Because there are two oxygen atoms, the compound is a dioxide. Thus the compound is chlorine dioxide. It is widely used as a substitute for chlorine in municipal water treatment plants because, unlike chlorine, it does not react with organic compounds in water to produce potentially toxic chlorinated compounds.

## Exercise 2.4.1

Write the name of each binary covalent compound.

1. $IF_7$
2. $N_2O_5$
3. $OF_2$

**Answer**

1. iodine heptafluoride
2. dinitrogen pentoxide
3. oxygen difluoride

## Example 2.4.2

Write the formula for each binary covalent compound.

1. sulfur trioxide
2. diiodine pentoxide

**Given:** name of compound

**Asked for:** formula

**Strategy:**

List the elements in the same order as in the formula, use Table 2.4.1 to identify the number of each type of atom present, and then indicate this quantity as a subscript to the right of that element when writing the formula.

**Solution**

1. Sulfur has no prefix, which means that each molecule has only one sulfur atom. The prefix *tri-* indicates that there are three oxygen atoms. The formula is therefore $SO_3$. Sulfur trioxide is produced industrially in huge amounts as an intermediate in the synthesis of sulfuric acid.
2. The prefix *di-* tells you that each molecule has two iodine atoms, and the prefix *penta-* indicates that there are five oxygen atoms. The formula is thus $I_2O_5$, a compound used to remove carbon monoxide from air in respirators.

**? Exercise 2.4.2**

Write the formula for each binary covalent compound.

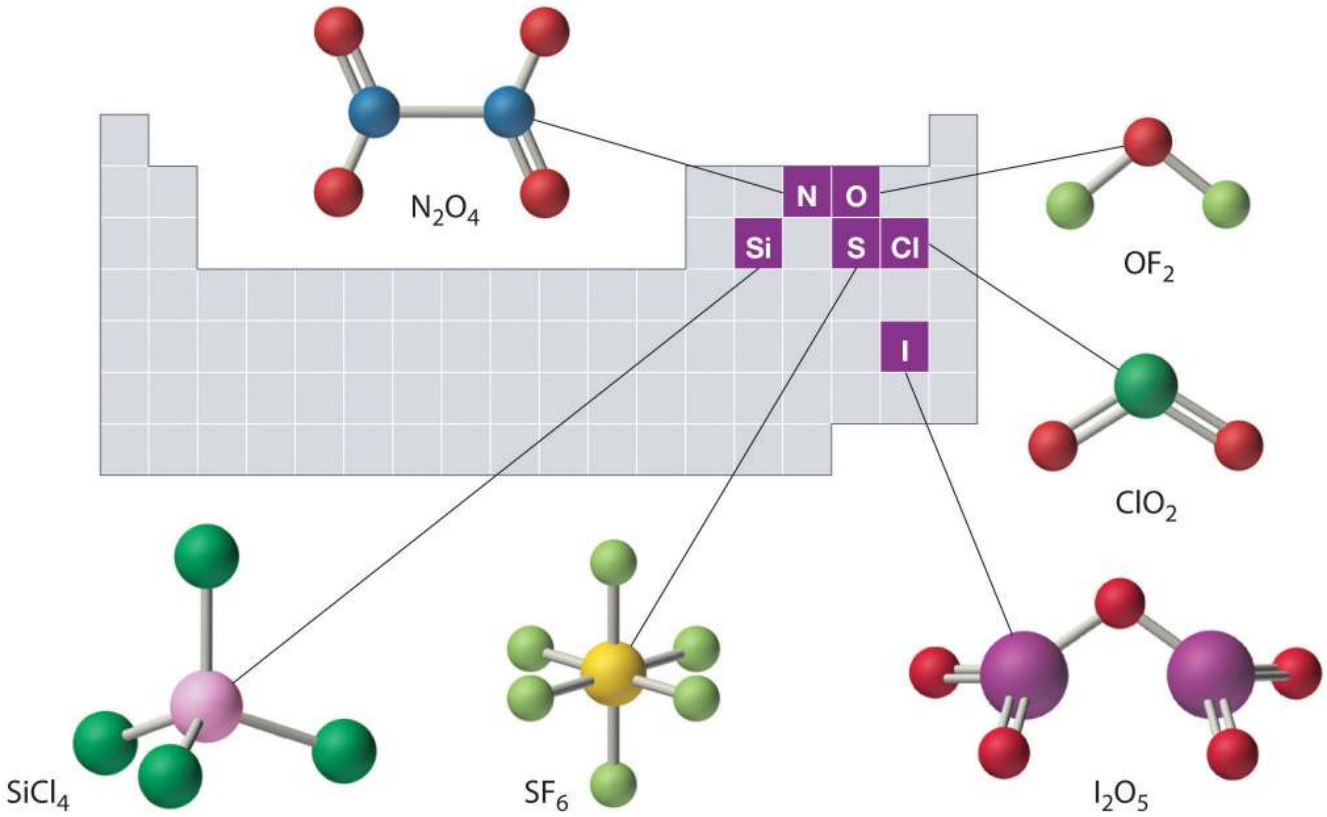
1. silicon tetrachloride
2. disulfur decafluoride

**Answer**

1. $SiCl_4$
2. $S_2F_{10}$

The structures of some of the compounds in Example 8 and Example 9 are shown in Figure 2.4.2 along with the location of the "central atom" of each compound in the periodic table. It may seem that the compositions and structures of such compounds are entirely random, but this is not true. After you have mastered the material in Chapter 7 and Chapter 8, you will be able to predict the compositions and structures of compounds of this type with a high degree of accuracy.

Figure 2.4.2 *The Structures of Some Covalent Inorganic Compounds and the Locations of the "Central Atoms" in the Periodic Table*



*The compositions and structures of covalent inorganic compounds are not random. As you will learn in Chapter 7 and Chapter 8, they can be predicted from the locations of the component atoms in the periodic table.*

## Hydrocarbons

Approximately one-third of the compounds produced industrially are organic compounds. All living organisms are composed of organic compounds, as is most of the food you consume, the medicines you take, the fibers in the clothes you wear, and the plastics in the materials you use. Section 2.1 introduced two organic compounds: methane ($CH_4$) and methanol ($CH_3OH$). These and other organic compounds appear frequently in discussions and examples throughout this text.

The detection of organic compounds is useful in many fields. In one recently developed application, scientists have devised a new method called “material degradomics” to make it possible to monitor the degradation of old books and historical documents. As paper ages, it produces a familiar “old book smell” from the release of organic compounds in gaseous form. The composition of the gas depends on the original type of paper used, a book’s binding, and the applied media. By analyzing these organic gases and isolating the individual components, preservationists are better able to determine the condition of an object and those books and documents most in need of immediate protection.

The simplest class of organic compounds is the **hydrocarbons**, which consist entirely of carbon and hydrogen. Petroleum and natural gas are complex, naturally occurring mixtures of many different hydrocarbons that furnish raw materials for the chemical industry. The four major classes of hydrocarbons are the **alkanes**, which contain only carbon–hydrogen and carbon–carbon single bonds; the **alkenes**, which contain at least one carbon–carbon double bond; the **alkynes**, which contain at least one carbon–carbon triple bond; and the **aromatic hydrocarbons**, which usually contain rings of six carbon atoms that can be drawn with alternating single and double bonds. Alkanes are also called *saturated* hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are *unsaturated*.

## Alkanes

The simplest alkane is methane ($CH_4$), a colorless, odorless gas that is the major component of natural gas. In larger alkanes whose carbon atoms are joined in an unbranched chain (*straight-chain alkanes*), each carbon atom is bonded to at most two other carbon atoms. The structures of two simple alkanes are shown in *Figure* 2.4.3, and the names and condensed structural formulas for the first 10 straight-chain alkanes are in Table 2.4.2. The names of all alkanes end in *-ane*, and their boiling points increase as the number of carbon atoms increases.

Figure 2.4.3 *Straight-Chain Alkanes with Two and Three Carbon Atoms*

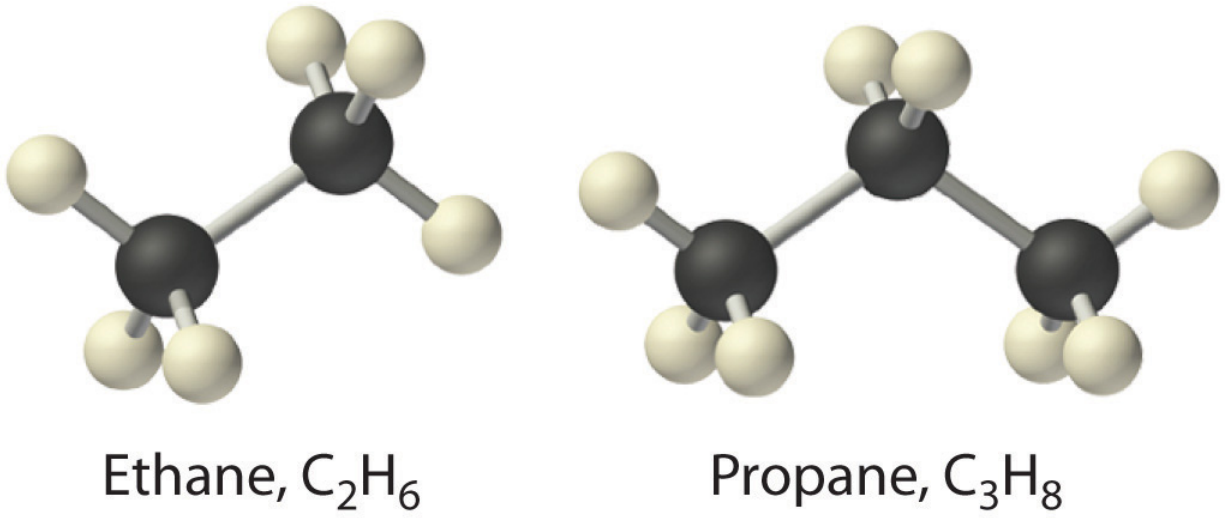
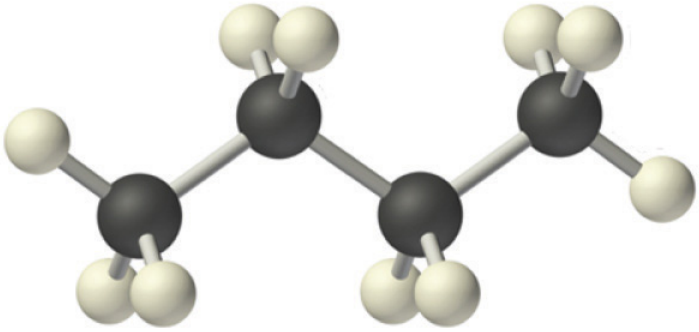


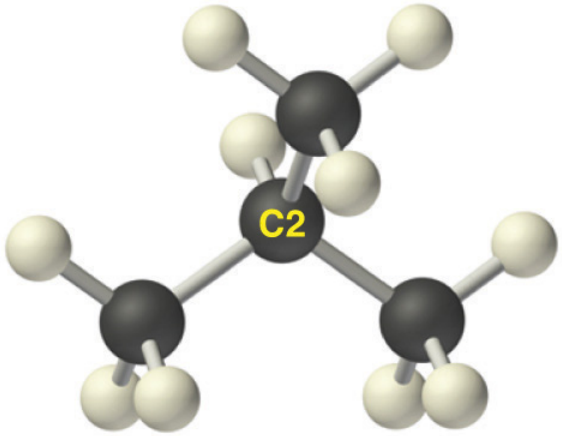

*Table* 2.4.2The First 10 Straight-Chain Alkanes

| Name | Number of Carbon Atoms | Molecular Formula | Condensed Structural Formula | Boiling Point (°C) | Uses |
|---|---|---|---|---|---|
| methane | 1 | $CH_4$ | $CH_4$ | −162 | natural gas constituent |
| ethane | 2 | $C_2H_6$ | $CH_3CH_3$ | −89 | natural gas constituent |
| propane | 3 | $C_3H_8$ | $CH_3CH_2CH_3$ | −42 | bottled gas |
| butane | 4 | $C_4H_{10}$ | $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$ | 0 | lighters, bottled gas |
| pentane | 5 | $C_5H_{12}$ | $CH_3(CH_2)_3CH_3$ | 36 | solvent, gasoline |
| hexane | 6 | $C_6H_{14}$ | $CH_3(CH_2)_4CH_3$ | 69 | solvent, gasoline |
| heptane | 7 | $C_7H_{16}$ | $CH_3(CH_2)_5CH_3$ | 98 | solvent, gasoline |
| octane | 8 | $C_8H_{18}$ | $CH_3(CH_2)_6CH_3$ | 126 | gasoline |
| nonane | 9 | $C_9H_{20}$ | $CH_3(CH_2)_7CH_3$ | 151 | gasoline |
| decane | 10 | $C_{10}H_{22}$ | $CH_3(CH_2)_8CH_3$ | 174 | kerosene |

Alkanes with four or more carbon atoms can have more than one arrangement of atoms. The carbon atoms can form a single unbranched chain, or the primary chain of carbon atoms can have one or more shorter chains that form branches. For example, butane ($C_4H_{10}$) has two possible structures. *Normal* butane (usually called *n*-butane) is $CH_3CH_2CH_2CH_3$, in which the carbon atoms form a single unbranched chain. In contrast, the condensed structural formula for *isobutane* is $(CH_3)_2CHCH_3$, in which the primary chain of three carbon atoms has a one-carbon chain branching at the central carbon. Three-dimensional representations of both structures are as follows:

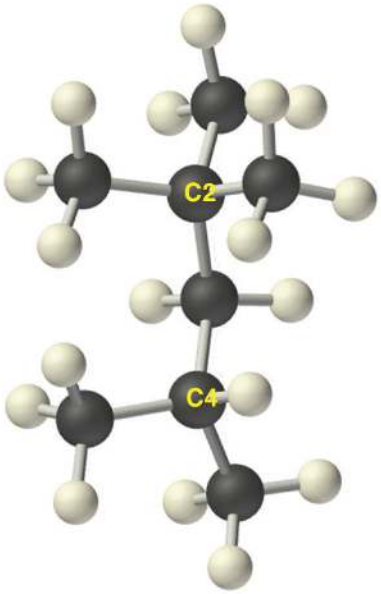


*n*-Butane, $C_4H_{10}$




Isobutane (2-methylpropane), $C_4H_{10}$

The systematic names for branched hydrocarbons use the lowest possible number to indicate the position of the branch along the longest straight carbon chain in the structure. Thus the systematic name for isobutane is 2-methylpropane, which indicates that a methyl group (a branch consisting of $–CH_3$) is attached to the second carbon of a propane molecule. Similarly, you will learn in Section 2.6 that one of the major components of gasoline is commonly called isooctane; its structure is as follows:




Isooctane (2,2,4-trimethylpentane)

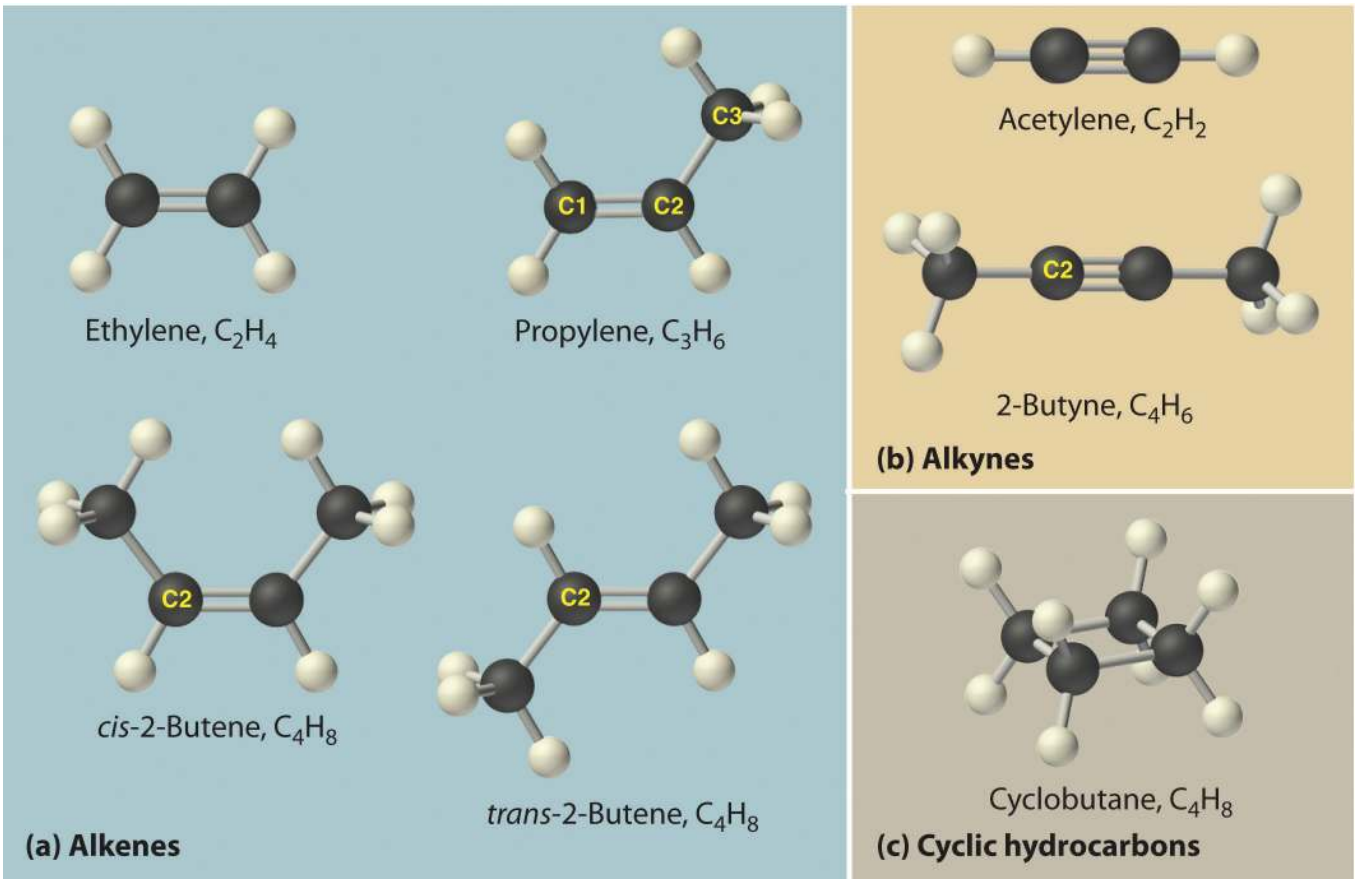
As you can see, the compound has a chain of five carbon atoms, so it is a derivative of pentane. There are two methyl group branches at one carbon atom and one methyl group at another. Using the lowest possible numbers for the branches gives 2,2,4-trimethylpentane for the systematic name of this compound.

## Alkenes

The simplest alkenes are *ethylene*, $C_2H_4$ or $CH_2{=}CH_2$, and *propylene*, $C_3H_6$ or $CH_3CH{=}CH_2$ (part (a) in Figure 2.16). The names of alkenes that have more than three carbon atoms use the same stems as the names of the alkanes (Table 2.7) but end in *-ene* instead of *-ane*.

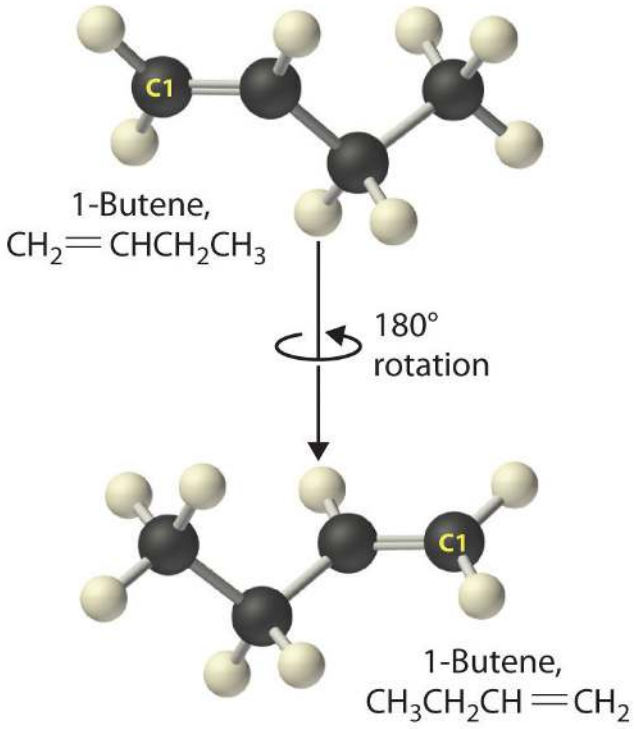
Once again, more than one structure is possible for alkenes with four or more carbon atoms. For example, an alkene with four carbon atoms has three possible structures. One is $CH_2{=}CHCH_2CH_3$ (1-butene), which has the double bond between the first and second carbon atoms in the chain. The other two structures have the double bond between the second and third carbon atoms and are forms of $CH_3CH{=}CHCH_3$ (2-butene). All four carbon atoms in 2-butene lie in the same plane, so there are two possible structures (part (a) in Figure 2.4.4 ). If the two methyl groups are on the same side of the double bond, the compound is *cis*-2-butene (from the Latin *cis*, meaning “on the same side”). If the two methyl groups are on opposite sides of the double bond, the compound is *trans*-2-butene (from the Latin *trans*, meaning “across”). These are distinctly different molecules: *cis*-2-butene melts at −138.9°C, whereas *trans*-2-butene melts at −105.5°C.

Figure 2.4.4 *Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons*




*The positions of the carbon atoms in the chain are indicated by C1 or C2.*

Just as a number indicates the positions of branches in an alkane, the number in the name of an alkene specifies the position of the *first* carbon atom of the double bond. The name is based on the lowest possible number starting from *either end* of the carbon chain, so $CH_3CH_2CH{=}CH_2$ is called 1-butene, *not* 3-butene. Note that $CH_2{=}CHCH_2CH_3$ and $CH_3CH_2CH{=}CH_2$ are different ways of writing the *same molecule* (1-butene) in two different orientations.




***The name of a compound does not depend on its orientation.*** *As illustrated for 1-butene, both condensed structural formulas and molecular models show different orientations of the same molecule. Don't let orientation fool you; you must be able to recognize the same structure no matter what its orientation.*

### Note the Pattern

The positions of groups or multiple bonds are always indicated by the lowest number possible.

## Alkynes

The simplest alkyne is *acetylene*, $C_2H_2$ or HC≡CH (part (b) in Figure 2.4.4 ). Because a mixture of acetylene and oxygen burns with a flame that is hot enough (>3000°C) to cut metals such as hardened steel, acetylene is widely used in cutting and welding torches. The names of other alkynes are similar to those of the corresponding alkanes but end in *-yne*. For example, $HC{\equiv}CCH_3$ is *propyne*, and $CH_3C{\equiv}CCH_3$ is *2-butyne* because the multiple bond begins on the second carbon atom.

### Note the Pattern

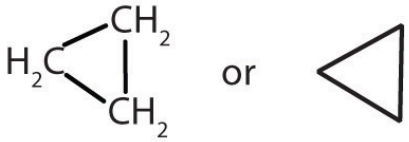
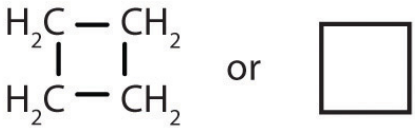
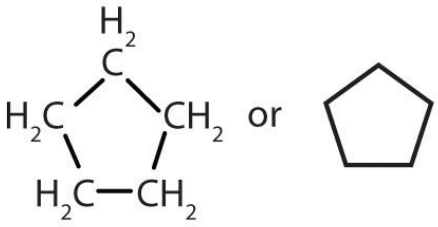
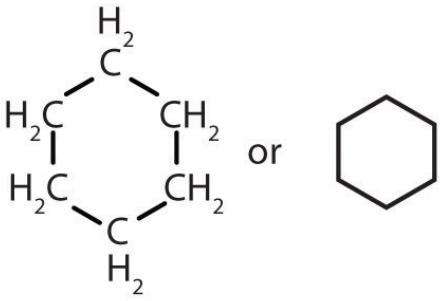
The number of bonds between carbon atoms in a hydrocarbon is indicated in the suffix:

- alk*ane*: only carbon–carbon single bonds
- alk*ene*: at least one carbon–carbon double bond
- alk*yne*: at least one carbon–carbon triple bond

## Cyclic Hydrocarbons

In a **cyclic hydrocarbon**, the ends of a hydrocarbon chain are connected to form a ring of covalently bonded carbon atoms. Cyclic hydrocarbons are named by attaching the prefix *cyclo-* to the name of the alkane, the alkene, or the alkyne. The simplest cyclic alkanes are *cyclopropane* ($C_3H_6$) a flammable gas that is also a powerful anesthetic, and *cyclobutane* ($C_4H_8$) (part (c) in Figure 2.4.4 ). The most common way to draw the structures of cyclic alkanes is to sketch a polygon with the same number of vertices as there are carbon atoms in the ring; each vertex represents a $CH_2$ unit. The structures of the cycloalkanes that contain three to six carbon atoms are shown schematically in Figure 2.4.5 .

Figure 2.4.5 *The Simple Cycloalkanes*

| Name | Molecular Formula | Structural Formula |
|---|---|---|
| cyclopropane | $C_3H_6$ |  |
| cyclobutane | $C_4H_8$ |  |
| cyclopentane | $C_5H_{10}$ |  |
| cyclohexane | $C_6H_{12}$ |  |

## Aromatic Hydrocarbons

Alkanes, alkenes, alkynes, and cyclic hydrocarbons are generally called **aliphatic hydrocarbons**. The name comes from the Greek *aleiphar*, meaning "oil," because the first examples were extracted from animal fats. In contrast, the first examples of **aromatic hydrocarbons**, also called *arenes*, were obtained by the distillation and degradation of highly scented (thus *aromatic*) resins from tropical trees.

The simplest aromatic hydrocarbon is *benzene* ($C_6H_6$), which was first obtained from a coal distillate. The word *aromatic* now refers to benzene and structurally similar compounds. As shown in part (a) in Figure 2.4.6, it is possible to draw the structure of benzene in two different but equivalent ways, depending on which carbon atoms are connected by double bonds or single bonds. *Toluene* is similar to benzene, except that one hydrogen atom is replaced by a $–CH_3$ group; it has the formula $C_7H_8$ (part (b) in Figure 2.4.6). As you will soon learn, the chemical behavior of aromatic compounds differs from the behavior of aliphatic compounds. Benzene and toluene are found in gasoline, and benzene is the starting material for preparing substances as diverse as aspirin and nylon.

Figure 2.4.6 *Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene*

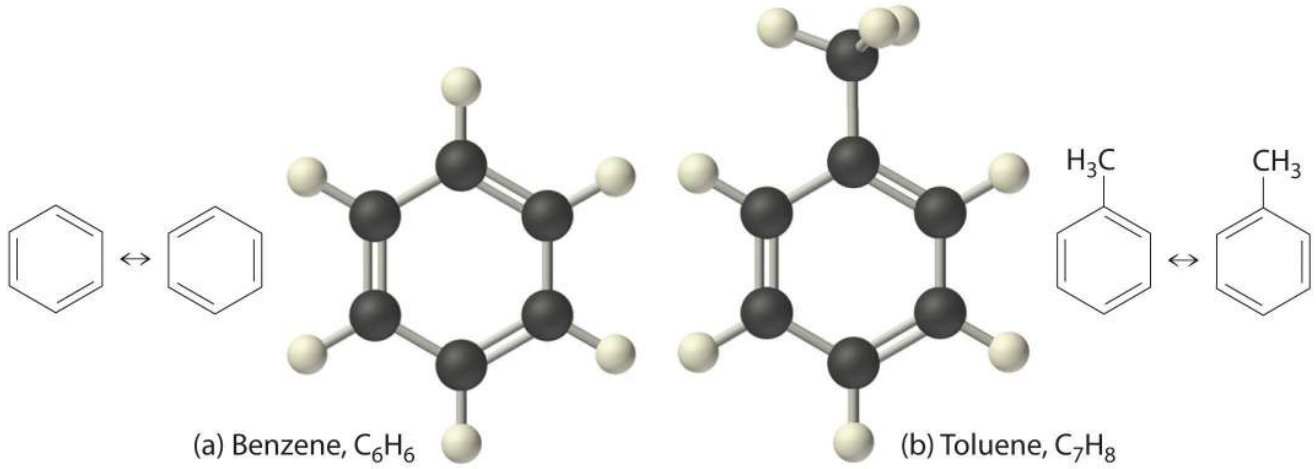
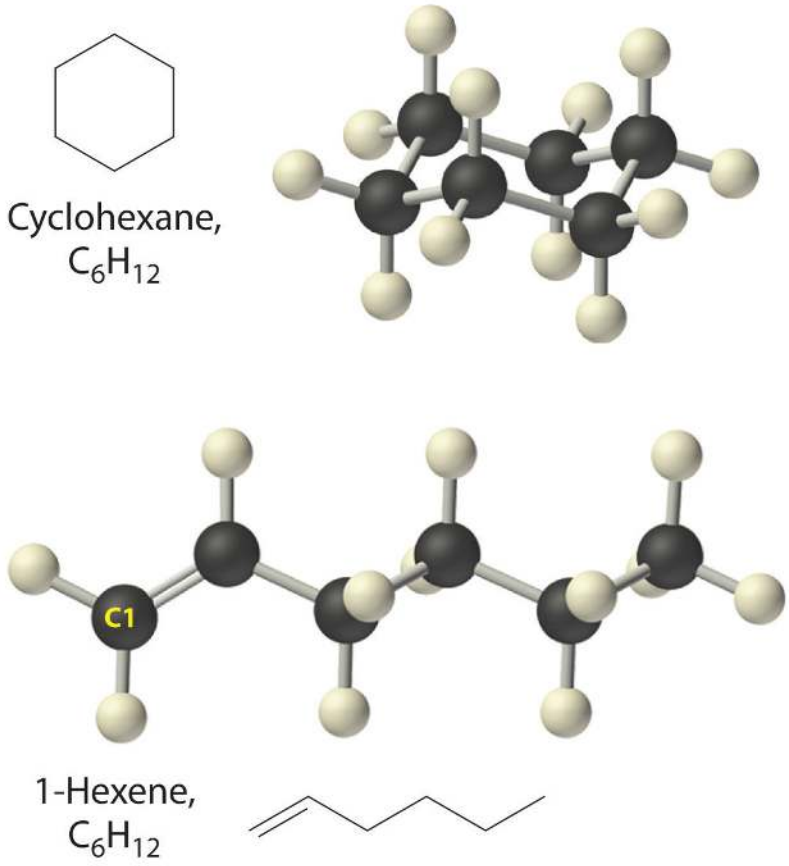



Figure 2.4.7 illustrates two of the molecular structures possible for hydrocarbons that have six carbon atoms. As you can see, compounds with the same molecular formula can have very different structures.

Figure 2.4.7 *Two Hydrocarbons with the Molecular Formula $C_6H_{12}$*




**Example 2.4.3**

Write the condensed structural formula for each hydrocarbon.

1. *n*-heptane
2. 2-pentene
3. 2-butyne


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4. cyclooctene

**Given:** name of hydrocarbon

**Asked for:** condensed structural formula

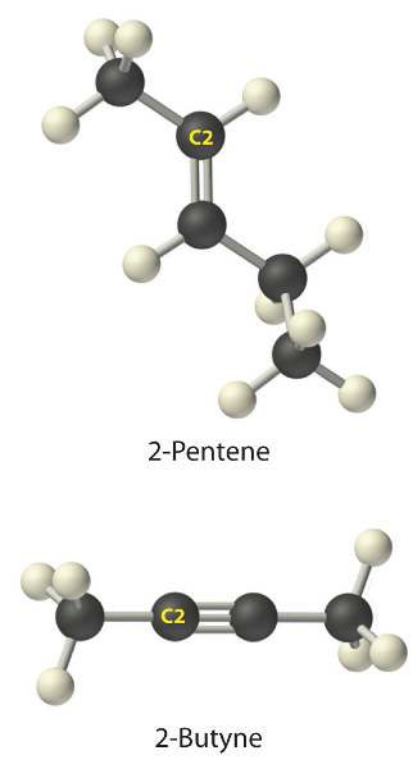
**Strategy:**

**A** Use the prefix to determine the number of carbon atoms in the molecule and whether it is cyclic. From the suffix, determine whether multiple bonds are present.

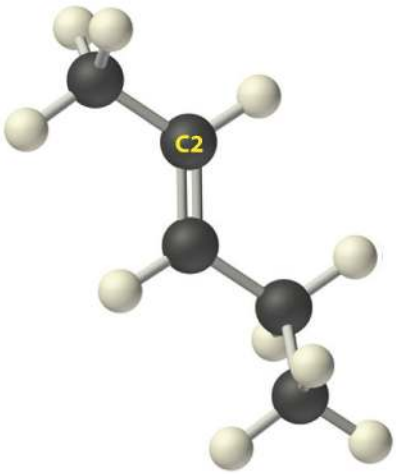
**B** Identify the position of any multiple bonds from the number(s) in the name and then write the condensed structural formula.

**Solution**

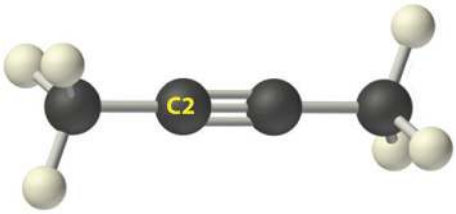
1. **A** The prefix *hept-* tells us that this hydrocarbon has seven carbon atoms, and *n-* indicates that the carbon atoms form a straight chain. The suffix *-ane* tells that it is an alkane, with no carbon–carbon double or triple bonds. **B** The condensed structural formula is $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$, which can also be written as $CH_3(CH_2)_5CH_3$.
2. **A** The prefix *pent-* tells us that this hydrocarbon has five carbon atoms, and the suffix *-ene* indicates that it is an alkene, with a carbon–carbon double bond. **B** The 2- tells us that the double bond begins on the second carbon of the five-carbon atom chain. The condensed structural formula of the compound is therefore $CH_3CH{=}CHCH_2CH_3$.




3. **A** The prefix *but-* tells us that the compound has a chain of four carbon atoms, and the suffix *-yne* indicates that it has a carbon–carbon triple bond. **B** The 2- tells us that the triple bond begins on the second carbon of the four-carbon atom chain. So the condensed structural formula for the compound is $CH_3C{\equiv}CCH_3$.

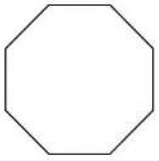



2-Pentene

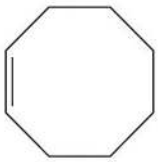



2-Butyne

4. **A** The prefix *cyclo-* tells us that this hydrocarbon has a ring structure, and *oct-* indicates that it contains eight carbon atoms, which we can draw as



The suffix *-ene* tells us that the compound contains a carbon–carbon double bond, but where in the ring do we place the double bond? **B** Because all eight carbon atoms are identical, it doesn't matter. We can draw the structure of cyclooctene as



## Exercise 2.4.3

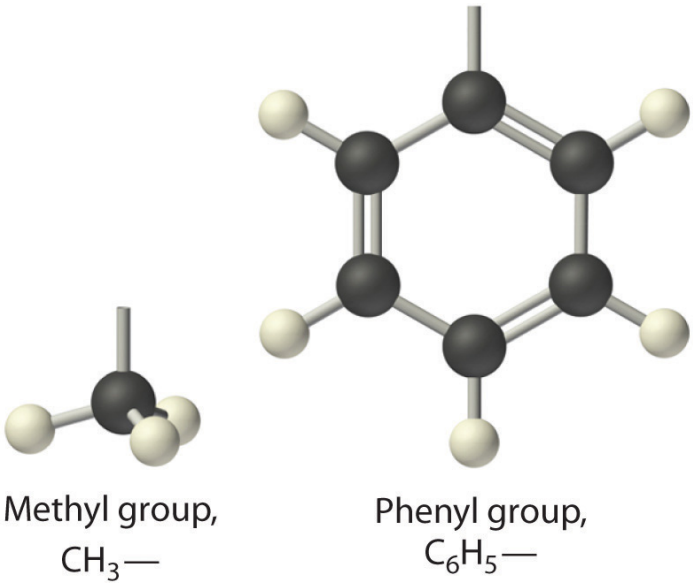
Write the condensed structural formula for each hydrocarbon.

1. *n*-octane
2. 2-hexene
3. 1-heptyne
4. cyclopentane

**Answer**

1. $CH_3(CH_2)_6CH_3$
2. $CH_3CH{=}CHCH_2CH_2CH_3$
3. $HC{\equiv}C(CH_2)_4CH_3$
4. 

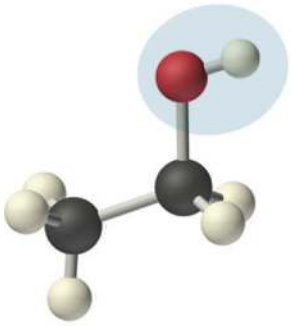
The general name for a group of atoms derived from an alkane is an *alkyl group*. The name of an alkyl group is derived from the name of the alkane by adding the suffix *-yl*. Thus the $–CH_3$ fragment is a *methyl* group, the $–CH_2CH_3$ fragment is an *ethyl* group, and so forth, where the dash represents a single bond to some other atom or group. Similarly, groups of atoms derived from aromatic hydrocarbons are *aryl groups*, which sometimes have unexpected names. For example, the $–C_6H_5$ fragment is derived from benzene, but it is called a *phenyl* group. In general formulas and structures, alkyl and aryl groups are often abbreviated as **R**.



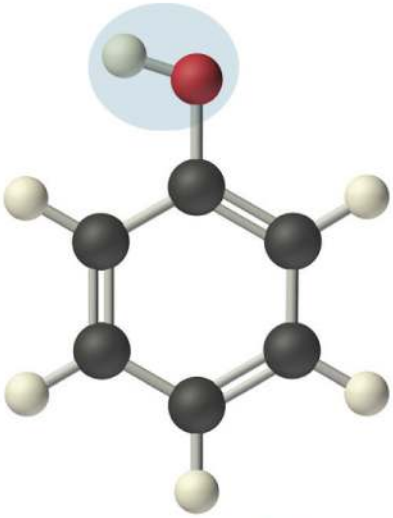

***Structures of alkyl and aryl groups.*** *The methyl group is an example of an alkyl group, and the phenyl group is an example of an aryl group.*

## Alcohols

Replacing one or more hydrogen atoms of a hydrocarbon with an –OH group gives an **alcohol**, represented as ROH. The simplest alcohol ($CH_3OH$) is called either *methanol* (its systematic name) or *methyl alcohol* (its common name) (see  "Different Ways of Representing the Structure of a Molecule"). Methanol is the antifreeze in automobile windshield washer fluids, and it is also used as an efficient fuel for racing cars, most notably in the Indianapolis 500. Ethanol (or ethyl alcohol, $CH_3CH_2OH$) is familiar as the alcohol in fermented or distilled beverages, such as beer, wine, and whiskey; it is also used as a gasoline additive (Section 2.6). The simplest alcohol derived from an aromatic hydrocarbon is $C_6H_5OH$, *phenol* (shortened from *phenyl* alcohol), a potent disinfectant used in some sore throat medications and mouthwashes.



Ethanol, $CH_3CH_2$**OH**



Phenol, $C_6H_5$**OH**

Ethanol, which is easy to obtain from fermentation processes, has successfully been used as an alternative fuel for several decades. Although it is a "green" fuel when derived from plants, it is an imperfect substitute for fossil fuels because it is less efficient than gasoline. Moreover, because ethanol absorbs water from the atmosphere, it can corrode an engine's seals. Thus other types of processes are being developed that use bacteria to create more complex alcohols, such as octanol, that are more energy efficient and that have a lower tendency to absorb water. As scientists attempt to reduce mankind's dependence on fossil fuels, the development of these so-called *biofuels* is a particularly active area of research.

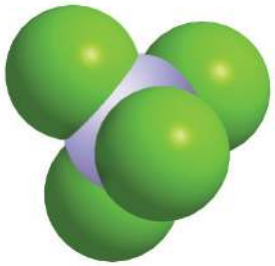
## Summary

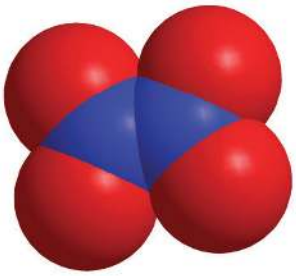
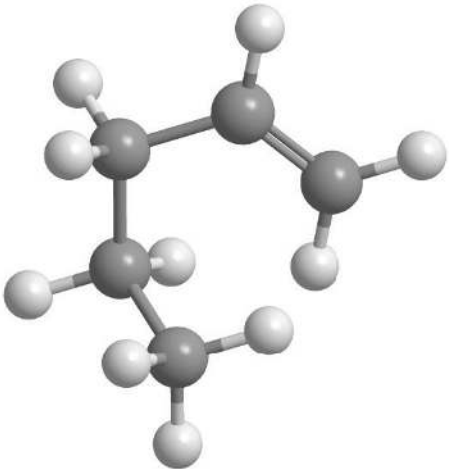
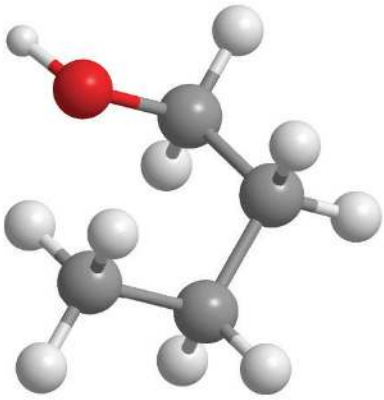
Covalent inorganic compounds are named by a procedure similar to that used for ionic compounds, using prefixes to indicate the numbers of atoms in the molecular formula. The simplest organic compounds are the **hydrocarbons**, which contain *only* carbon and hydrogen. **Alkanes** contain only carbon–hydrogen and carbon–carbon single bonds, **alkenes** contain at least one carbon–carbon double bond, and **alkynes** contain one or more carbon–carbon triple bonds. Hydrocarbons can also be **cyclic**, with the ends of the chain connected to form a ring. Collectively, alkanes, alkenes, and alkynes are called **aliphatic hydrocarbons**. **Aromatic hydrocarbons**, or *arenes*, are another important class of hydrocarbons that contain rings of carbon atoms related to the structure of benzene ($C_6H_6$). A derivative of an alkane or an arene from which one hydrogen atom has been removed is called an *alkyl group* or an *aryl group*, respectively. **Alcohols** are another common class of organic compound, which contain an –OH group covalently bonded to either an alkyl group or an aryl group (often abbreviated **R**).

## KEY TAKEAWAY

- Covalent inorganic compounds are named using a procedure similar to that used for ionic compounds, whereas hydrocarbons use a system based on the number of bonds between carbon atoms.

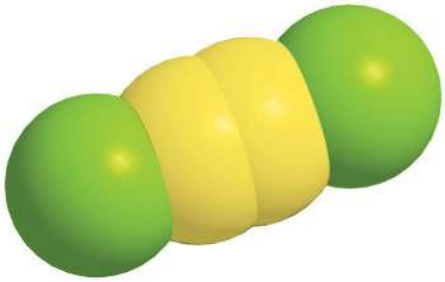
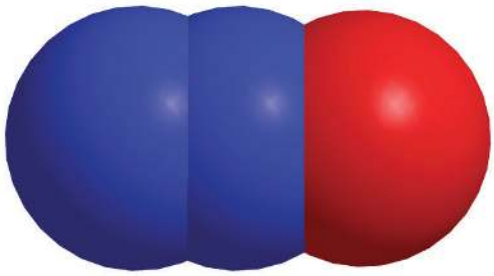
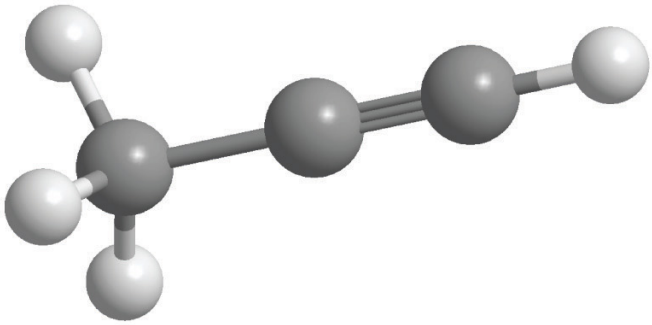
## CONCEPTUAL PROBLEMS

1. Benzene ($C_6H_6$) is an organic compound, and KCl is an ionic compound. The sum of the masses of the atoms in each empirical formula is approximately the same. How would you expect the two to compare with regard to each of the following? What species are present in benzene vapor?
    1. melting point
    2. type of bonding
    3. rate of evaporation
    4. structure
2. Can an inorganic compound be classified as a hydrocarbon? Why or why not?
3. Is the compound $NaHCO_3$ a hydrocarbon? Why or why not?
4. Name each compound.
    1. NiO
    2. $TiO_2$
    3. $N_2O$
    4. $CS_2$
    5. $SO_3$
    6. $NF_3$
    7. $SF_6$
5. Name each compound.
    1. $HgCl_2$
    2. $IF_5$
    3. $N_2O_5$
    4. $Cl_2O$
    5. HgS
    6. $PCl_5$
6. For each structural formula, write the condensed formula and the name of the compound.
    1. 
    2. 

3. 
4. 
5. 

7. For each structural formula, write the condensed formula and the name of the compound.

1. 

2. 
3. 
4. 

8. Would you expect $PCl_3$ to be an ionic compound or a covalent compound? Explain your reasoning.
9. What distinguishes an aromatic hydrocarbon from an aliphatic hydrocarbon?
10. The following general formulas represent specific classes of hydrocarbons. Refer to *Table* 2.4.2 and Figure 2.4.4 and identify the classes.
    1. $C_nH_{2n+2}$
    2. $C_nH_{2n}$
    3. $C_nH_{2n-2}$
11. Using R to represent an alkyl or aryl group, show the general structure of an
    1. alcohol.
    2. phenol.

## Answer

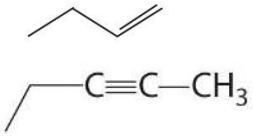
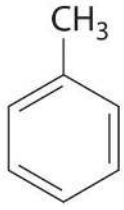
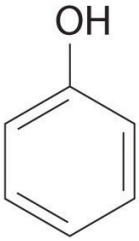
1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. 1. ROH (where R is an alkyl group)

2. ROH (where R is an aryl group)

## NUMERICAL PROBLEMS

1. Write the formula for each compound.
    1. dinitrogen monoxide
    2. silicon tetrafluoride
    3. boron trichloride
    4. nitrogen trifluoride
    5. phosphorus tribromide
2. Write the formula for each compound.
    1. dinitrogen trioxide
    2. iodine pentafluoride
    3. boron tribromide
    4. oxygen difluoride
    5. arsenic trichloride
3. Write the formula for each compound.
    1. thallium(I) selenide
    2. neptunium(IV) oxide
    3. iron(II) sulfide
    4. copper(I) cyanide
    5. nitrogen trichloride
4. Name each compound.
    1. $RuO_4$
    2. $PbO_2$
    3. $MoF_6$
    4. $Hg_2(NO_3)_2 \cdot 2H_2O$
    5. $WCl_4$
5. Name each compound.
    1. $NbO_2$
    2. $MoS_2$
    3. $P_4S_{10}$
    4. $Cu_2O$
    5. $ReF_5$
6. Draw the structure of each compound.
    1. propyne
    2. ethanol
    3. *n*-hexane
    4. cyclopropane
    5. benzene
7. Draw the structure of each compound.
    1. 1-butene
    2. 2-pentyne
    3. cycloheptane
    4. toluene
    5. phenol

## AnswerS

1. 1. $N_2O$
   2. $SiF_4$
   3. $BCl_3$
   4. $NF_3$
   5. $PBr_3$
2. 
3. 1. $Tl_2Se$
   2. $NpO_2$
   3. FeS
   4. CuCN
   5. $NCl_3$
4. 
5. 1. niobium (IV) oxide
   2. molybdenum (IV) sulfide
   3. tetraphosphorus decasulfide
   4. copper(I) oxide
   5. rhenium(V) fluoride
6. 
7. 1. 
   2. 
   3. 
   4. 
   5. –

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# 2.5: Acids and Bases

**Learning Objectives**

- To identify and name some common acids and bases.

For our purposes at this point in the text, we can define an **acid** as a substance with at least one hydrogen atom that can dissociate to form an anion and an $H^+$ ion (a proton) in aqueous solution, thereby forming an *acidic solution*. We can define **bases** as compounds that produce hydroxide ions ($OH^-$) and a For cation when dissolved in water, thus forming a *basic solution*. Solutions that are neither basic nor acidic are *neutral*. We will discuss the chemistry of acids and bases in more detail in Chapter 4, Chapter 8, and Chapter 16, but in this section we describe the nomenclature of common acids and identify some important bases so that you can recognize them in future discussions. Pure acids and bases and their concentrated aqueous solutions are commonly encountered in the laboratory. They are usually highly corrosive, so they must be handled with care.

## Acids

The names of acids differentiate between (1) acids in which the $H^+$ ion is attached to an oxygen atom of a polyatomic anion (these are called **oxoacids**, or occasionally **oxyacids**) and (2) acids in which the $H^+$ ion is attached to some other element. In the latter case, the name of the acid begins with *hydro-* and ends in *-ic*, with the root of the name of the other element or ion in between. Recall that the name of the anion derived from this kind of acid always ends in *-ide*. Thus hydrogen chloride (HCl) gas dissolves in water to form hydrochloric acid (which contains $H^+$ and $Cl^-$ ions), hydrogen cyanide (HCN) gas forms hydrocyanic acid (which contains $H^+$ and $CN^-$ ions), and so forth (Table 2.5.1 ). Examples of this kind of acid are commonly encountered and very important. For instance, your stomach contains a dilute solution of hydrochloric acid to help digest food. When the mechanisms that prevent the stomach from digesting itself malfunction, the acid destroys the lining of the stomach and an ulcer forms.

### Note the Pattern

Acids are distinguished by whether the $H^+$ ion is attached to an oxygen atom of a polyatomic anion or some other element.

Table 2.5.1 Some Common Acids That Do Not Contain Oxygen

| Formula | Name in Aqueous Solution | Name of Gaseous Species |
|---|---|---|
| HF | hydrofluoric acid | hydrogen fluoride |
| HCl | hydrochloric acid | hydrogen chloride |
| HBr | hydrobromic acid | hydrogen bromide |
| HI | hydroiodic acid | hydrogen iodide |
| HCN | hydrocyanic acid | hydrogen cyanide |
| $H_2S$ | hydrosulfuric acid | hydrogen sulfide |

If an acid contains one or more $H^+$ ions attached to oxygen, it is a derivative of one of the common oxoanions, such as sulfate ($SO_4^{2-}$) or nitrate ($NO_3^-$). These acids contain as many $H^+$ ions as are necessary to balance the negative charge on the anion, resulting in a neutral species such as $H_2SO_4$ and $HNO_3$.

The names of acids are derived from the names of anions according to the following rules:

1. **If the name of the anion ends in *-ate*, then the name of the acid ends in *-ic*.** For example, because $NO_3^-$ is the nitrate ion, $HNO_3$ is nitric acid. Similarly, $ClO_4^-$ is the perchlorate ion, so $HClO_4$ is perchloric acid. Two important acids are sulfuric acid ($H_2SO_4$) from the sulfate ion ($SO_4^{2-}$) and phosphoric acid ($H_3PO_4$) from the phosphate ion ($PO_4^{3-}$). These two names use a slight variant of the root of the anion name: *sulf*ate becomes *sulfur*ic and *phosph*ate becomes *phosphor*ic.
2. **If the name of the anion ends in *-ite*, then the name of the acid ends in *-ous*.** For example, $OCl^-$ is the hypochlorite ion, and HOCl is hypochlorous acid; $NO_2^-$ is the nitrite ion, and $HNO_2$ is nitrous acid; and $SO_3^{2-}$ is the sulfite ion, and $H_2SO_3$ is

sulfurous acid. The same roots are used whether the acid name ends in *-ic* or *-ous*; thus, *sulfite* becomes *sulfurous*.

The relationship between the names of the oxoacids and the parent oxoanions is illustrated in Figure 2.5.1, and some common oxoacids are in Table 2.5.2.

Figure 2.5.1 *The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions*

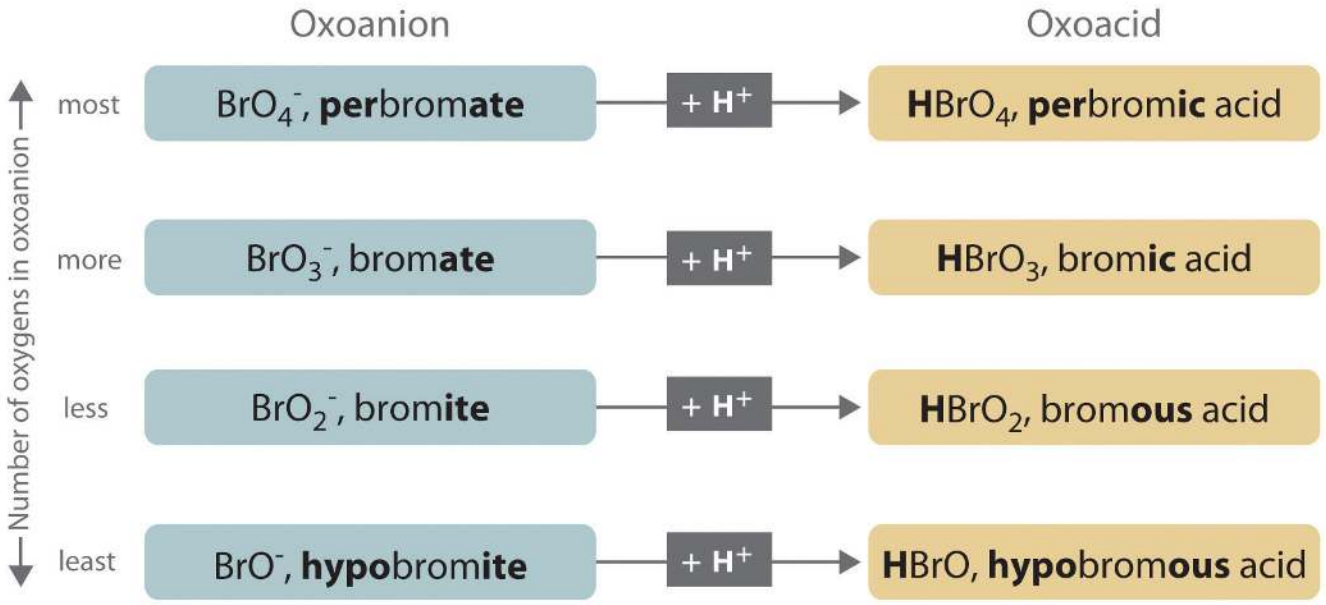



Table 2.5.2 Some Common Oxoacids

| Formula | Name |
|---|---|
| $HNO_2$ | nitrous acid |
| $HNO_3$ | nitric acid |
| $H_2SO_3$ | sulfurous acid |
| $H_2SO_4$ | sulfuric acid |
| $H_3PO_4$ | phosphoric acid |
| $H_2CO_3$ | carbonic acid |
| HClO | hypochlorous acid |
| $HClO_2$ | chlorous acid |
| $HClO_3$ | chloric acid |
| $HClO_4$ | perchloric acid |

**Example 2.5.1**

Name and give the formula for each acid.

1. the acid formed by adding a proton to the hypobromite ion ($OBr^-$)
2. the acid formed by adding two protons to the selenate ion ($SeO_4^{2-}$)

**Given:** anion

**Asked for:** parent acid

**Strategy:**

Refer to Table 2.5.1 and Table 2.5.2 to find the name of the acid. If the acid is not listed, use the guidelines given previously.

**Solution**

Neither species is listed in Table 2.5.1" or Table 2.5.2, so we must use the information given previously to derive the name of the acid from the name of the polyatomic anion.

1. The anion name, *hypobromite*, ends in *-ite*, so the name of the parent acid ends in *-ous*. The acid is therefore hypobromous acid (HOBr).
2. *Selenate* ends in *-ate*, so the name of the parent acid ends in *-ic*. The acid is therefore selenic acid ($H_2SeO_4$).

.

**? Exercise 2.5.1**

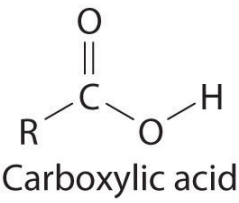
Name and give the formula for each acid.

1. the acid formed by adding a proton to the perbromate ion ($BrO_4^-$)
2. the acid formed by adding three protons to the arsenite ion ($AsO_3^{3-}$)

**Answer**

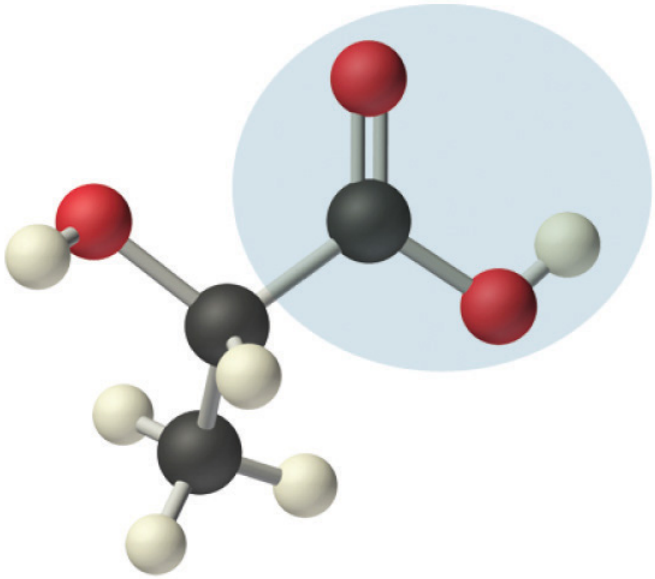
1. perbromic acid; $HBrO_4$
2. arsenous acid; $H_3AsO_3$

Many organic compounds contain the **carbonyl group**, in which there is a carbon–oxygen double bond. In **carboxylic acids**, an –OH group is covalently bonded to the carbon atom of the carbonyl group. Their general formula is $RCO_2H$, sometimes written as RCOOH:



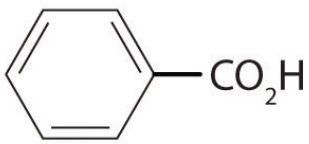
Carboxylic acid

where R can be an alkyl group, an aryl group, or a hydrogen atom. The simplest example, $HCO_2H$, is *formic acid*, so called because it is found in the secretions of stinging ants (from the Latin *formica*, meaning “ant”). Another example is *acetic acid* ($CH_3CO_2H$), which is found in vinegar. Like many acids, carboxylic acids tend to have sharp odors. For example, butyric acid ($CH_3CH_2CH_2CO_2H$), is responsible for the smell of rancid butter, and the characteristic odor of sour milk and vomit is due to lactic acid [$CH_3CH(OH)CO_2H$]. Some common carboxylic acids are shown in Figure 2.5.2.



Lactic acid, $CH_3CH(OH)\mathbf{CO_2H}$

Figure 2.5.2*Some Common Carboxylic Acids*

| Formula (Structure) | Name | Uses |
|---|---|---|
| $HCO_2H$ | formic acid | tanning, dyeing |
| $CH_3CO_2H$ | acetic acid | vinegar, food preservative |
| $CH_3CH_2CO_2H$ | propionic acid | food preservative |
| $CH_3CH_2CH_2CO_2H$ | butyric acid | varnishes |
| $C_6H_5CO_2H$  | benzoic acid | food preservative, dyeing |

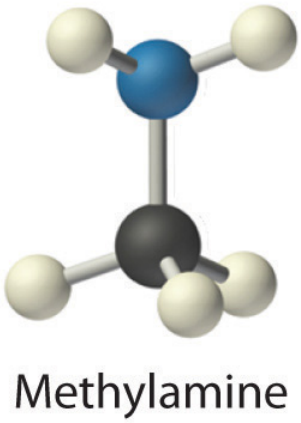
Although carboxylic acids are covalent compounds, when they dissolve in water, they dissociate to produce $H^+$ ions (just like any other acid) and $RCO_2^-$ ions. Note that *only the hydrogen attached to the oxygen atom of the $CO_2$ group dissociates to form an $H^+$ ion*. In contrast, the hydrogen atom attached to the oxygen atom of an alcohol does *not* dissociate to form an $H^+$ ion when an alcohol is dissolved in water. The reasons for the difference in behavior between carboxylic acids and alcohols will be discussed in Chapter 8.

### Note the Pattern

Only the hydrogen attached to the oxygen atom of the $CO_2$ group dissociates to form an $H^+$ ion.

## Bases

We will present more comprehensive definitions of bases in later chapters, but virtually every base you encounter in the meantime will be an ionic compound, such as sodium hydroxide (NaOH) and barium hydroxide [$Ba(OH)_2$], that contain the hydroxide ion and a metal cation. These have the general formula $M(OH)_n$. It is important to recognize that alcohols, with the general formula ROH, are covalent compounds, not ionic compounds; consequently, they do *not* dissociate in water to form a basic solution (containing $OH^-$ ions). When a base reacts with any of the acids we have discussed, it accepts a proton ($H^+$). For example, the hydroxide ion ($OH^-$) accepts a proton to form $H_2O$. Thus bases are also referred to as *proton acceptors*.




Concentrated aqueous solutions of ammonia ($NH_3$) contain significant amounts of the hydroxide ion, even though the dissolved substance is *not* primarily ammonium hydroxide ($NH_4OH$) as is often stated on the label. Thus aqueous ammonia solution is also a common base. Replacing a hydrogen atom of $NH_3$ with an alkyl group results in an **amine** ($RNH_2$), which is also a base. Amines have pungent odors—for example, methylamine ($CH_3NH_2$) is one of the compounds responsible for the foul odor associated with spoiled fish. The physiological importance of amines is suggested in the word *vitamin*, which is derived from the phrase *vital amines*. The word was coined to describe dietary substances that were effective at preventing scurvy, rickets, and other diseases because these substances were assumed to be amines. Subsequently, some vitamins have indeed been confirmed to be amines.

### Note the Pattern

Metal hydroxides (MOH) yield $OH^-$ ions and are bases, alcohols (ROH) do not yield $OH^-$ or $H^+$ ions and are neutral, and carboxylic acids ($RCO_2H$) yield $H^+$ ions and are acids.

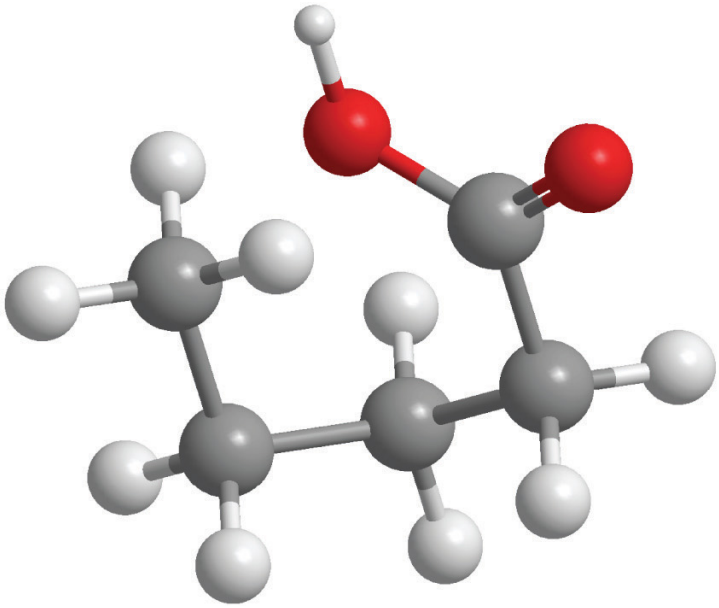
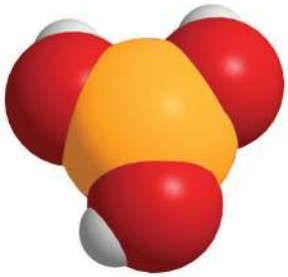
### Summary

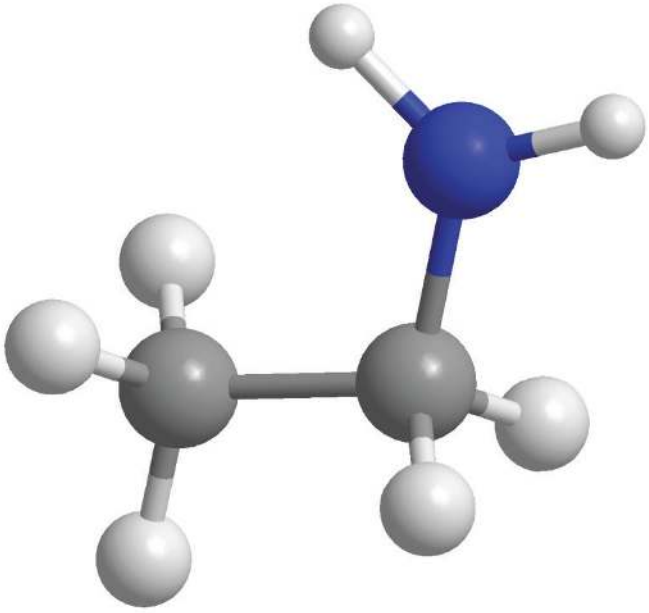
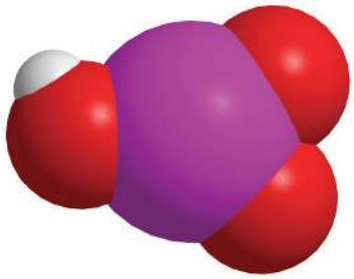
Common **acids** and the polyatomic anions derived from them have their own names and rules for nomenclature. The nomenclature of acids differentiates between **oxoacids**, in which the $H^+$ ion is attached to an oxygen atom of a polyatomic ion, and acids in which the $H^+$ ion is attached to another element. **Carboxylic acids** are an important class of organic acids. Ammonia is an important **base**, as are its organic derivatives, the **amines**.

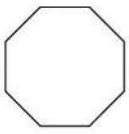
### KEY TAKEAWAY

- Common acids and polyatomic anions derived from them have their own names and rules for nomenclature.

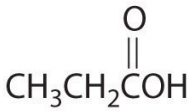
## CONCEPTUAL PROBLEMS

1. Name each acid.
    1. HCl
    2. $HBrO_3$
    3. $HNO_3$
    4. $H_2SO_4$
    5. $HIO_3$
2. Name each acid.
    1. HBr
    2. $H_2SO_3$
    3. $HClO_3$
    4. HCN
    5. $H_3PO_4$
3. Name the aqueous acid that corresponds to each gaseous species.
    1. hydrogen bromide
    2. hydrogen cyanide
    3. hydrogen iodide
4. For each structural formula, write the condensed formula and the name of the compound.
    1. 
    2. 
5. For each structural formula, write the condensed formula and the name of the compound.

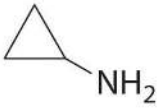
1. 
2. 

6. When each compound is added to water, is the resulting solution acidic, neutral, or basic?
    1. $CH_3CH_2OH$
    2. $Mg(OH)_2$
    3. $C_6H_5CO_2H$
    4. LiOH
    5. $C_3H_7CO_2H$
    6. $H_2SO_4$
7. Draw the structure of the simplest example of each type of compound.
    1. alkane
    2. alkene
    3. alkyne
    4. aromatic hydrocarbon
    5. alcohol
    6. carboxylic acid
    7. amine
    8. cycloalkane
8. Identify the class of organic compound represented by each compound.
    1. 
    2. $CH_3CH_2OH$

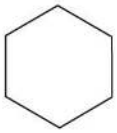
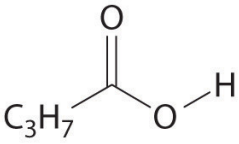
3. $HC{\equiv}CH$
4. 
5. $C_3H_7NH_2$
6. $CH_3CH{=}CHCH_2CH_3$
7. 

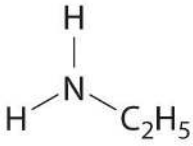
8. 

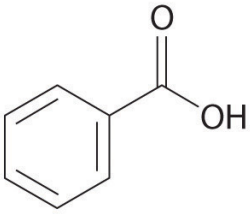

9. Identify the class of organic compound represented by each compound.

1. 

2. 

3. 
4. 
5. 

6. $CH_3C{\equiv}CH$
7. 

8. 


## NUMERICAL PROBLEMS

1. Write the formula for each compound.
    1. hypochlorous acid

2. perbromic acid
3. hydrobromic acid
4. sulfurous acid
5. sodium perbromate

2. Write the formula for each compound.
    1. hydroiodic acid
    2. hydrogen sulfide
    3. phosphorous acid
    4. perchloric acid
    5. calcium hypobromite
3. Name each compound.
    1. HBr
    2. $H_2SO_3$
    3. HCN
    4. $HClO_4$
    5. $NaHSO_4$
4. Name each compound.
    1. $H_2SO_4$
    2. $HNO_2$
    3. $K_2HPO_4$
    4. $H_3PO_3$
    5. $Ca(H_2PO_4)_2 \cdot H_2O$

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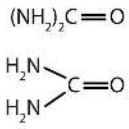
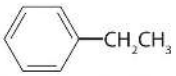
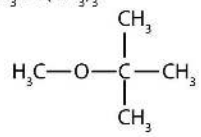
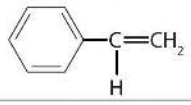
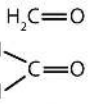
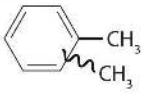
# 2.6: Industrially Important Chemicals

**Learning Objectives**

- To appreciate the scope of the chemical industry and its contributions to modern society.

It isn't easy to comprehend the scale on which the chemical industry must operate to supply the huge amounts of chemicals required in modern industrial societies. Figure 2.6.1 lists the names and formulas of the chemical industry's "top 25" for 2002—the 25 chemicals produced in the largest quantity in the United States that year—along with the amounts produced, in *billions* of pounds. To put these numbers in perspective, consider that the 88.80 billion pounds of sulfuric acid produced in the United States in 2002 has a volume of 21.90 million cubic meters ($2.19 \times 10^7$ $m^3$), enough to fill the Pentagon, probably the largest office building in the world, about 22 times.

Figure 2.6.1 *Top 25 Chemicals Produced in the United States in 2002**

| Rank | Name | Formula (Structure) | Billions of Pounds |
|---|---|---|---|
| 1 | sulfuric acid | $H_2SO_4$ | 88.80 |
| 2 | nitrogen | $N_2$ | 58.70 |
| 3 | oxygen | $O_2$ | 42.38 |
| 4 | ethylene | $H_2C{=}CH_2$ | 40.41 |
| 5 | ammonia | $NH_3$ | 35.95 |
| 6 | calcium oxide (lime) | CaO | 34.72 |
| 7 | phosphoric acid | $H_3PO_4$ | 25.36 |
| 8 | sodium hydroxide | NaOH | 24.02 |
| 9 | propylene (propene) | $CH_3CH{=}CH_2$ | 22.60 |
| 10 | chlorine | $Cl_2$ | 22.28 |
| 11 | sodium carbonate | $Na_2CO_3$ | 20.89 |
| 12 | urea | $(NH_2)_2C{=}O$  | 16.84 |
| 13 | nitric acid | $HNO_3$ | 16.08 |
| 14 | 1,2-dichloroethane (ethylene dichloride) | $ClCH_2CH_2Cl$ | 15.94 |
| 15 | ammonium nitrate | $NH_4NO_3$ | 15.33 |
| 16 | vinyl chloride | $CH_2{=}CHCl$ | 13.23 |
| 17 | benzene | $C_6H_6$ | 12.01 |
| 18 | ethylbenzene | $C_6H_5CH_2CH_3$  | 10.99 |
| 19 | carbon dioxide | $CO_2$ | 10.91 |
| 20 | methyl *t*-butyl ether | $CH_3OC(CH_3)_3$  | 10.86 |
| 21 | styrene | $C_6H_5CH{=}CH_2$  | 8.94 |
| 22 | methanol | $CH_3OH$ | 8.73 |
| 23 | formaldehyde | $H_2C{=}O$  | 6.98 |
| 24 | xylenes (mixture)† | $(CH_3)_2C_6H_4$  | 6.38 |
| 25 | toluene | $C_6H_5CH_3$ | 6.03 |

*Nonlinear structures not previously introduced are shown with their respective formulas.
†The squiggly line indicates that the second —$CH_3$ group can be attached to any of the other positions of the ring.

According to Figure 2.6.1, 11 of the top 15 compounds produced in the United States are inorganic, and the total mass of inorganic chemicals produced is almost twice the mass of organic chemicals. Yet the diversity of organic compounds used in industry is such that over half of the top 25 compounds (13 out of 25) are organic.

Why are such huge quantities of chemical compounds produced annually? They are used both directly as components of compounds and materials that we encounter on an almost daily basis and indirectly in the production of those compounds and materials. The single largest use of industrial chemicals is in the production of foods: 7 of the top 15 chemicals are either fertilizers

(ammonia, urea, and ammonium nitrate) or used primarily in the production of fertilizers (sulfuric acid, nitric acid, nitrogen, and phosphoric acid). Many of the organic chemicals on the list are used primarily as ingredients in the plastics and related materials that are so prevalent in contemporary society. Ethylene and propylene, for example, are used to produce polyethylene and polypropylene, which are made into plastic milk bottles, sandwich bags, indoor-outdoor carpets, and other common items. Vinyl chloride, in the form of polyvinylchloride, is used in everything from pipes to floor tiles to trash bags. Though not listed in Figure 2.6.1, butadiene and carbon black are used in the manufacture of synthetic rubber for tires, and phenol and formaldehyde are ingredients in plywood, fiberglass, and many hard plastic items.

We do not have the space in this text to consider the applications of all these compounds in any detail, but we will return to many of them after we have developed the concepts necessary to understand their underlying chemistry. Instead, we conclude this chapter with a brief discussion of petroleum refining as it relates to gasoline and octane ratings and a look at the production and use of the topmost industrial chemical, sulfuric acid.

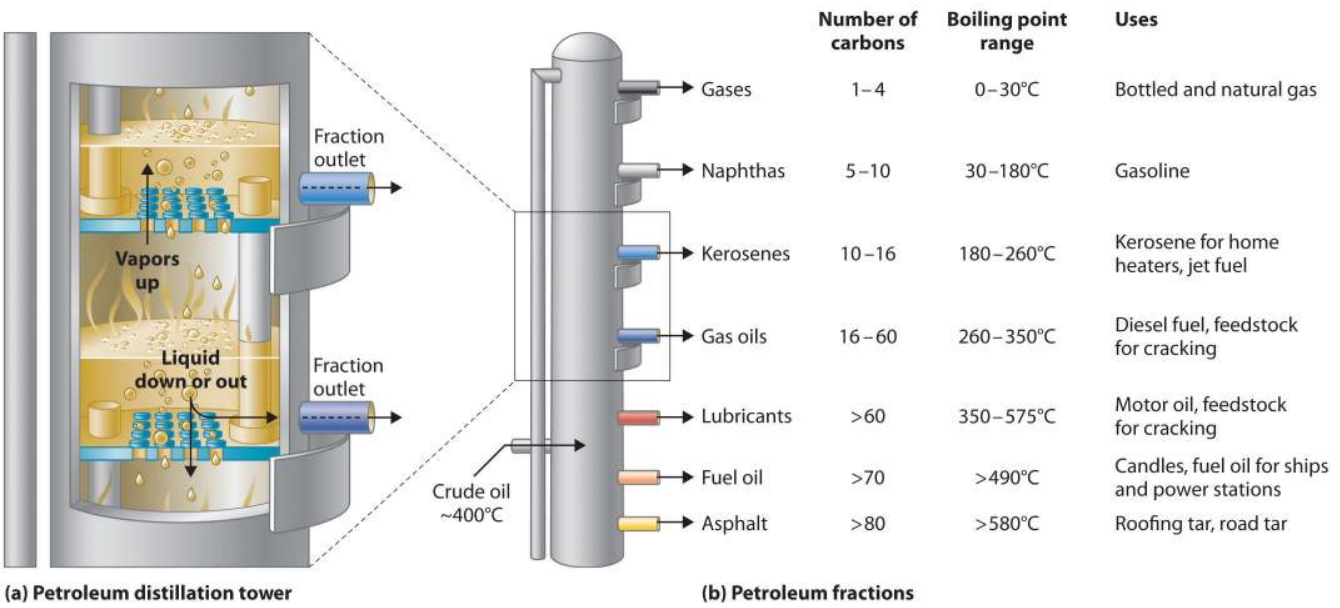
## Petroleum

The petroleum that is pumped out of the ground at locations around the world is a complex mixture of several thousand organic compounds, including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. The identities and relative abundances of the components vary depending on the source. So Texas crude oil is somewhat different from Saudi Arabian crude oil. In fact, the analysis of petroleum from different deposits can produce a "fingerprint" of each, which is useful in tracking down the sources of spilled crude oil. For example, Texas crude oil is "sweet," meaning that it contains a small amount of sulfur-containing molecules, whereas Saudi Arabian crude oil is "sour," meaning that it contains a relatively large amount of sulfur-containing molecules.

## Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Recall from Chapter 1 that distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure 2.6.2 shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the *feedstock*, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in \Figure 2.6.2)shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

Figure 2.6.2 *The Distillation of Petroleum*



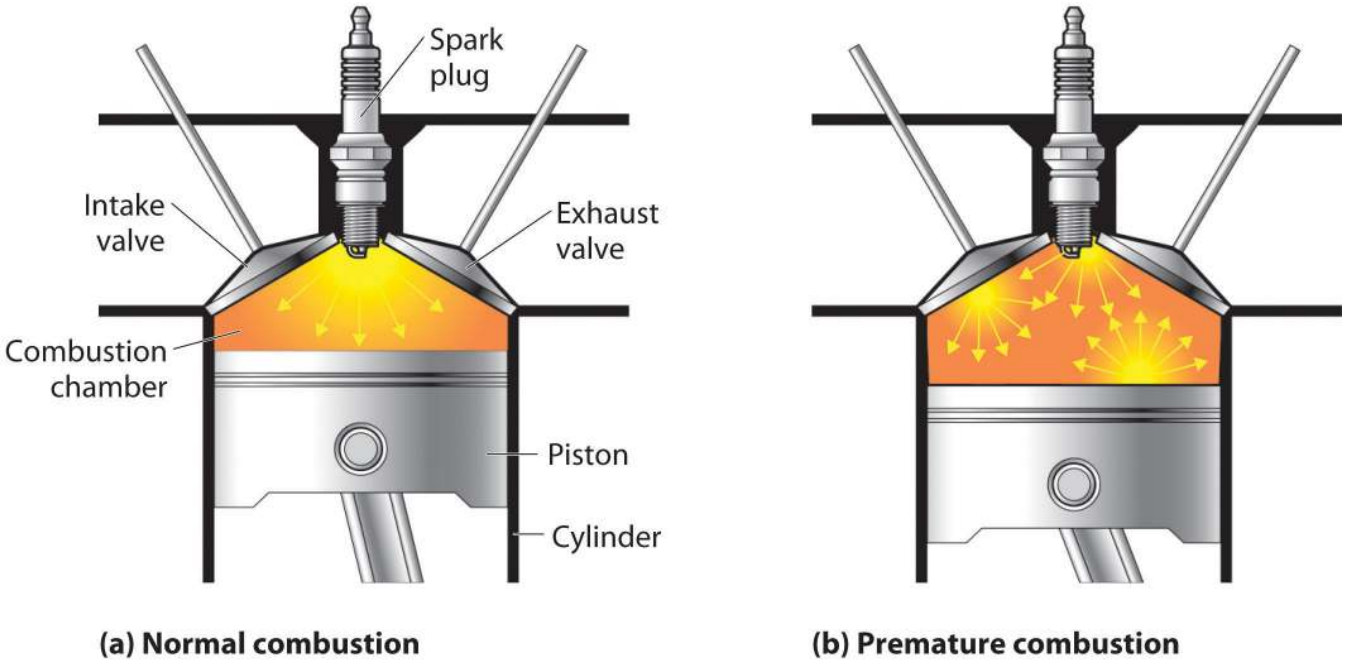

*(a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

The economics of petroleum refining are complex. For example, the market demand for kerosene and lubricants is much lower than the demand for gasoline, yet all three fractions are obtained from the distillation column in comparable amounts. Furthermore, most gasolines and jet fuels are blends with very carefully controlled compositions that cannot vary as their original feedstocks did. To make petroleum refining more profitable, the less volatile, lower-value fractions must be converted to more volatile, higher-value mixtures that have carefully controlled formulas. The first process used to accomplish this transformation is **cracking**, in which the larger and heavier hydrocarbons in the kerosene and higher-boiling-point fractions are heated to temperatures as high as 900°C. High-temperature reactions cause the carbon–carbon bonds to break, which converts the compounds to lighter molecules similar to those in the gasoline fraction. Thus in cracking, a straight-chain alkane with a number of carbon atoms corresponding to the kerosene fraction is converted to a mixture of hydrocarbons with a number of carbon atoms corresponding to the lighter gasoline fraction. The second process used to increase the amount of valuable products is called **reforming**; it is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons. Using metals such as platinum brings about the necessary chemical reactions. The mixtures of products obtained from cracking and reforming are separated by fractional distillation.

## Octane Ratings

The quality of a fuel is indicated by its **octane rating**, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 2.6.3), which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

Figure 2.6.3 *The Burning of Gasoline in an Internal Combustion Engine*




*(a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

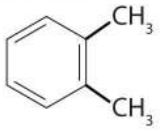
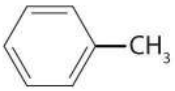
The octane scale was established in 1927 using a standard test engine and two pure compounds: *n*-heptane and isooctane (2,2,4-trimethylpentane). *n*-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of *n*-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% *n*-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89$$

A gasoline that performs at the same level as a blend of 89% isooctane and 11% *n*-heptane is assigned an octane rating of 89; this represents an intermediate grade of gasoline. Regular gasoline typically has an octane rating of 87; premium has a rating of 93 or higher.

As shown in Figure 2.6.4 many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead [$(C_2H_5)_4Pb$], which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic. Other enhancers, such as methyl *t*-butyl ether (MTBE), have been developed to take their place. They combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

Figure 2.6.4 *The Octane Ratings of Some Hydrocarbons and Common Additives*

| Name | Condensed Structural Formula | Octane Rating | Name | Condensed Structural Formula | Octane Rating |
|---|---|---|---|---|---|
| *n*-heptane | $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ | 0 | *o*-xylene |  | 107 |
| *n*-hexane | $CH_3CH_2CH_2CH_2CH_2CH_3$ | 25 | ethanol | $CH_3CH_2OH$ | 108 |
| *n*-pentane | $CH_3CH_2CH_2CH_2CH_3$ | 62 | *t*-butyl alcohol | $(CH_3)_3COH$ | 113 |
| isooctane | $(CH_3)_3CCH_2CH(CH_3)_2$ | 100 | *p*-xylene |  | 116 |
| benzene |  | 106 | methyl *t*-butyl ether | $H_3COC(CH_3)_3$ | 116 |
| methanol | $CH_3OH$ | 107 | toluene |  | 118 |

## Example 2.6.1

You have a crude (i.e., unprocessed or *straight-run*) petroleum distillate consisting of 10% *n*-heptane, 10% *n*-hexane, and 80% *n*-pentane by mass, with an octane rating of 52. What percentage of MTBE by mass would you need to increase the octane rating of the distillate to that of regular-grade gasoline (a rating of 87), assuming that the octane rating is directly proportional to the amounts of the compounds present? Use the information presented in Figure 2.6.4.

**Given:** composition of petroleum distillate, initial octane rating, and final octane rating

**Asked for:** percentage of MTBE by mass in final mixture

**Strategy:**

**A** Define the unknown as the percentage of MTBE in the final mixture. Then subtract this unknown from 100% to obtain the percentage of petroleum distillate.

**B** Multiply the percentage of MTBE and the percentage of petroleum distillate by their respective octane ratings; add these values to obtain the overall octane rating of the new mixture.

**C** Solve for the unknown to obtain the percentage of MTBE needed.

**Solution**

**A** The question asks what percentage of MTBE will give an overall octane rating of 87 when mixed with the straight-run fraction. From Figure 2.6.4, the octane rating of MTBE is 116. Let $x$ be the percentage of MTBE, and let $100 - x$ be the percentage of petroleum distillate.

**B** Multiplying the percentage of each component by its respective octane rating and setting the sum equal to the desired octane rating of the mixture (87) times 100 gives

final octane rating of mixture $=87(100)=52(100-x)+116x=5200-52x+116x=5200+64x$

**C** Solving the equation gives $x = 55\%$. Thus the final mixture must contain 55% MTBE by mass.

To obtain a composition of 55% MTBE by mass, you would have to add more than an equal mass of MTBE (actually 0.55/0.45, or 1.2 times) to the straight-run fraction. This is 1.2 tons of MTBE per ton of straight-run gasoline, which would be

prohibitively expensive. Thus there are sound economic reasons for reforming the kerosene fractions to produce toluene and other aromatic compounds, which have high octane ratings and are much cheaper than MTBE.

**? Exercise 2.6.1**

As shown in Figure 2.6.4, toluene is one of the fuels suitable for use in automobile engines. How much toluene would have to be added to a blend of the petroleum fraction in this example containing 15% MTBE by mass to increase the octane rating to that of premium gasoline (93)?

**Answer**

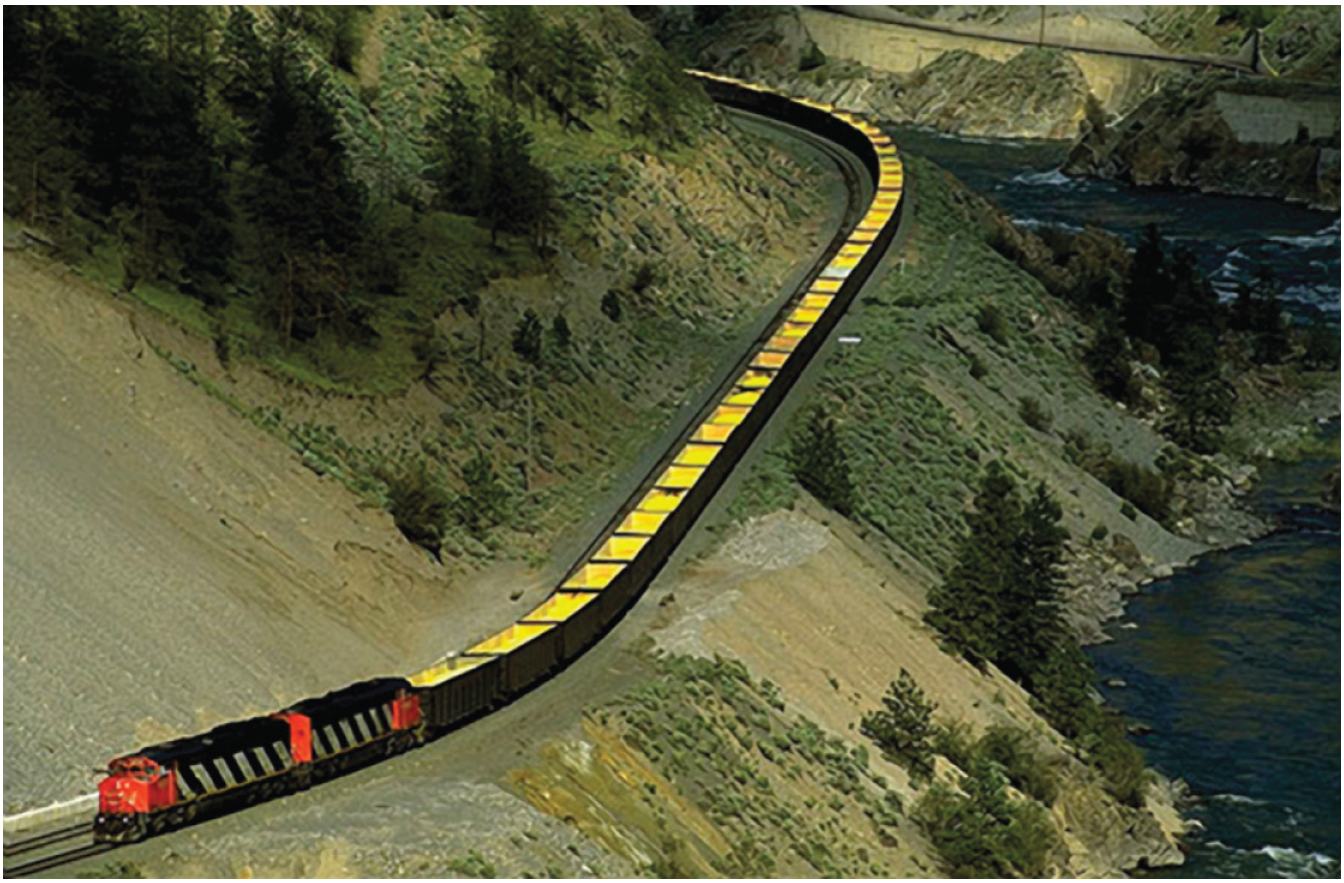
The final blend is 56% toluene by mass, which requires a ratio of 56/44, or 1.3 tons of toluene per ton of blend.

## Sulfuric Acid

Sulfuric acid is one of the oldest chemical compounds known. It was probably first prepared by alchemists who burned sulfate salts such as $FeSO_4 \cdot 7H_2O$, called green vitriol from its color and glassy appearance (from the Latin *vitrum*, meaning “glass”). Because pure sulfuric acid was found to be useful for dyeing textiles, enterprising individuals looked for ways to improve its production. By the mid-18th century, sulfuric acid was being produced in multiton quantities by the *lead-chamber process*, which was invented by John Roebuck in 1746. In this process, sulfur was burned in a large room lined with lead, and the resulting fumes were absorbed in water.

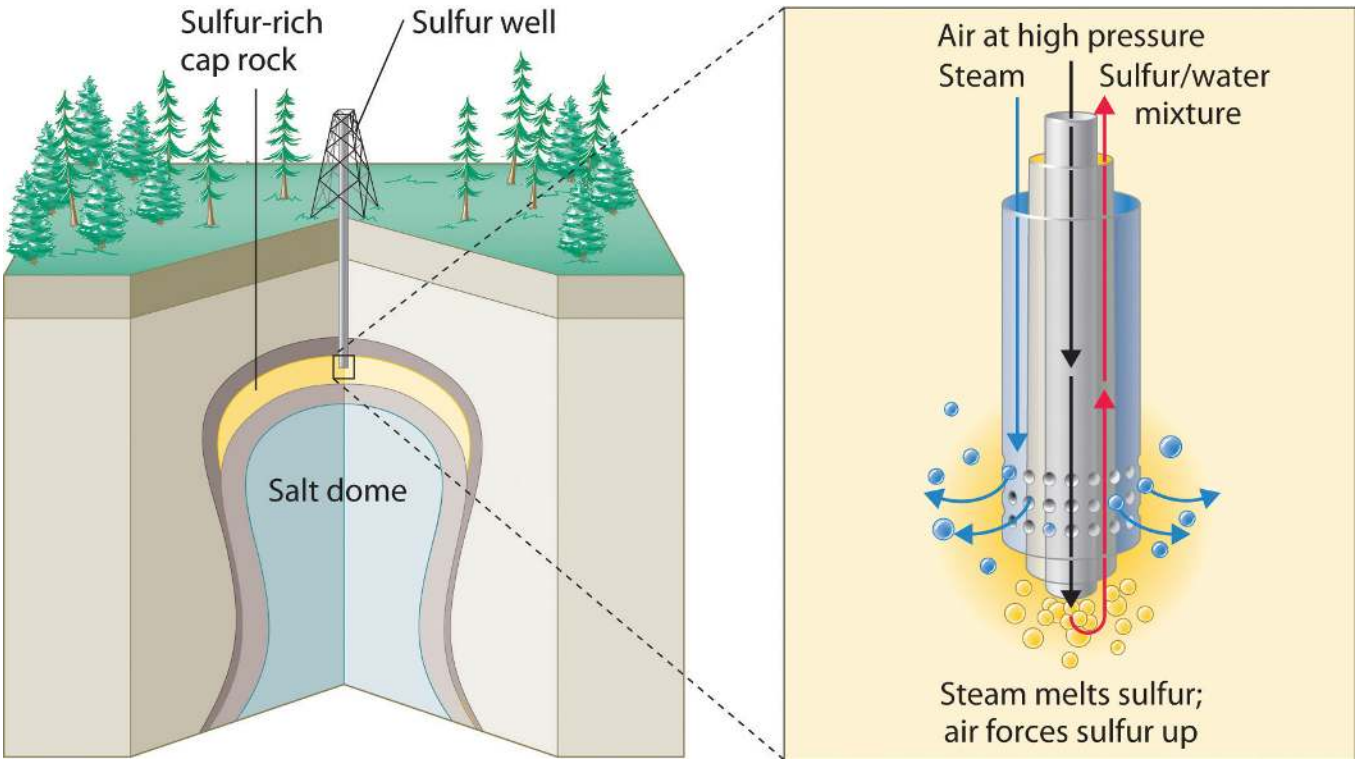
## Production

The production of sulfuric acid today is likely to start with elemental sulfur obtained through an ingenious technique called the *Frasch process*, which takes advantage of the low melting point of elemental sulfur (115.2°C). Large deposits of elemental sulfur are found in porous limestone rocks in the same geological formations that often contain petroleum. In the Frasch process, water at high temperature (160°C) and high pressure is pumped underground to melt the sulfur, and compressed air is used to force the liquid sulfur-water mixture to the surface (Figure 2.6.5. The material that emerges from the ground is more than 99% pure sulfur. After it solidifies, it is pulverized and shipped in railroad cars to the plants that produce sulfuric acid, as shown here.



***Transporting sulfur.*** *A train carries elemental sulfur through the White Canyon of the Thompson River in British Columbia, Canada.*

Figure 2.6.5 *Extraction of Elemental Sulfur from Underground Deposits*




*In the Frasch process for extracting sulfur, very hot water at high pressure is injected into the sulfur-containing rock layer to melt the sulfur. The resulting mixture of liquid sulfur and hot water is forced up to the surface by compressed air.*

An increasing number of sulfuric acid manufacturers have begun to use sulfur dioxide ($SO_2$) as a starting material instead of elemental sulfur. Sulfur dioxide is recovered from the burning of oil and gas, which contain small amounts of sulfur compounds. When not recovered, $SO_2$ is released into the atmosphere, where it is converted to an environmentally hazardous form that leads to *acid rain* (Chapter 4).

If sulfur is the starting material, the first step in the production of sulfuric acid is the combustion of sulfur with oxygen to produce $SO_2$. Next, $SO_2$ is converted to $SO_3$ by the *contact process*, in which $SO_2$ and $O_2$ react in the presence of $V_2O_5$ to achieve about 97% conversion to $SO_3$. The $SO_3$ can then be treated with a small amount of water to produce sulfuric acid. Usually, however, the $SO_3$ is absorbed in concentrated sulfuric acid to produce *oleum*, a more potent form called *fuming sulfuric acid*. Because of its high $SO_3$ content (approximately 99% by mass), oleum is cheaper to ship than concentrated sulfuric acid. At the point of use, the oleum is diluted with water to give concentrated sulfuric acid (*very carefully* because dilution generates enormous amounts of heat). Because $SO_2$ is a pollutant, the small amounts of unconverted $SO_2$ are recovered and recycled to minimize the amount released into the air.

## Uses

Two-thirds of the sulfuric acid produced in the United States is used to make fertilizers, most of which contain nitrogen, phosphorus, and potassium (in a form called *potash*). In earlier days, phosphate-containing rocks were simply ground up and spread on fields as fertilizer, but the extreme insolubility of many salts that contain the phosphate ion ($PO_4^{3-}$) limits the availability of phosphorus from these sources. Sulfuric acid serves as a source of protons ($H^+$ ions) that react with phosphate minerals to produce more soluble salts containing $HPO_4^{2-}$ or $H_2PO_4^-$ as the anion, which are much more readily taken up by plants. In this context, sulfuric acid is used in two principal ways: (1) the phosphate rocks are treated with concentrated sulfuric acid to produce "superphosphate," a mixture of 32% $CaHPO_4$ and $Ca(H_2PO_4)_2{\cdot}H_2O$, 50% $CaSO_4{\cdot}2H_2O$, approximately 3% absorbed phosphoric acid, and other nutrients; and (2) sulfuric acid is used to produce phosphoric acid ($H_3PO_4$), which can then be used to convert phosphate rocks to "triple superphosphate," which is largely $Ca(H_2PO_4)_2{\cdot}H_2O$.

Sulfuric acid is also used to produce potash, one of the other major ingredients in fertilizers. The name *potash* originally referred to potassium carbonate (obtained by boiling wood *ash*es with water in iron *pot*s), but today it also refers to compounds such as

potassium hydroxide (KOH) and potassium oxide ($K_2O$). The usual source of potassium in fertilizers is actually potassium sulfate ($K_2SO_4$), which is produced by several routes, including the reaction of concentrated sulfuric acid with solid potassium chloride (KCl), which is obtained as the pure salt from mineral deposits.

## Summary

Many chemical compounds are prepared industrially in huge quantities and used to produce foods, fuels, plastics, and other such materials. Petroleum refining takes a complex mixture of naturally occurring hydrocarbons as a feedstock and, through a series of steps involving distillation, **cracking**, and **reforming**, converts them to mixtures of simpler organic compounds with desirable properties. A major use of petroleum is in the production of motor fuels such as gasoline. The performance of such fuels in engines is described by their **octane rating**, which depends on the identity of the compounds present and their relative abundance in the blend.

Sulfuric acid is the compound produced in the largest quantity in the industrial world. Much of the sulfur used in the production of sulfuric acid is obtained via the Frasch process, in which very hot water forces liquid sulfur out of the ground in nearly pure form. Sulfuric acid is produced by the reaction of sulfur dioxide with oxygen in the presence of vanadium(V) oxide (the contact process), followed by absorption of the sulfur trioxide in concentrated sulfuric acid to produce oleum. Most sulfuric acid is used to prepare fertilizers.

## KEY TAKEAWAY

- Many chemical compounds are prepared industrially in huge quantities to prepare the materials we need and use in our daily lives.

## CONCEPTUAL PROBLEMS

1. Describe the processes used for converting crude oil to transportation fuels.
2. If your automobile engine is knocking, is the octane rating of your gasoline too low or too high? Explain your answer.
3. Tetraethyllead is no longer used as a fuel additive to prevent knocking. Instead, fuel is now marketed as “unleaded.” Why is tetraethyllead no longer used?
4. If you were to try to extract sulfur from an underground source, what process would you use? Describe briefly the essential features of this process.
5. Why are phosphate-containing minerals used in fertilizers treated with sulfuric acid?

## Answer

1.
2.
3.
4.
5. Phosphate salts contain the highly-charged $PO_4^{3-}$ ion, salts of which are often insoluble. Protonation of the $PO_4^{3-}$ ion by strong acids such as $H_2SO_4$ leads to the formation of the $HPO_4^{2-}$ and $H_2PO_4^-$ ions. Because of their decreased negative charge, salts containing these anions are usually much more soluble, allowing the anions to be readily taken up by plants when they are applied as fertilizer.

## NUMERICAL PROBLEM

1. In Example 2.6.1, the crude petroleum had an overall octane rating of 52. What is the composition of a solution of MTBE and *n*-heptane that has this octane rating?

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# CHAPTER OVERVIEW

## 3: Chemical Reactions


3.1: The Mole and Molar Masses
3.2: Determining Empirical and Molecular Formulas
3.3: Chemical Equations
3.4: Mass Relationships in Chemical Equations
3.5: Types of Chemical Reactions
3.6: Chemical Reactions in the Atmosphere
3.7: Essential Skills 2



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# 3.1: The Mole and Molar Masses

**Learning Objectives**

- To calculate the molecular mass of a covalent compound and the formula mass of an ionic compound and to calculate the number of atoms, molecules, or formula units in a sample of a substance.

As you learned in Chapter 1, the **mass number** is the sum of the numbers of protons and neutrons present in the nucleus of an atom. The mass number is an integer that is approximately equal to the numerical value of the atomic mass. Although the mass number is unitless, it is assigned units called **atomic mass units (amu)**. Because a molecule or a polyatomic ion is an assembly of atoms whose identities are given in its molecular or ionic formula, we can calculate the average atomic mass of any molecule or polyatomic ion from its composition by adding together the masses of the constituent atoms. The average mass of a monatomic ion is the same as the average mass of an atom of the element because the mass of electrons is so small that it is insignificant in most calculations.

## Molecular and Formula Masses

The **molecular mass** of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example 1.

**Example 3.1.1**

Calculate the molecular mass of ethanol, whose condensed structural formula is $CH_3CH_2OH$. Among its many uses, ethanol is a fuel for internal combustion engines.

**Given:** molecule

**Asked for:** molecular mass

**Strategy:**

**A** Determine the number of atoms of each element in the molecule.

**B** Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

**C** Add together the masses to give the molecular mass.

**Solution**

**A** The molecular formula of ethanol may be written in three different ways: $CH_3CH_2OH$ (which illustrates the presence of an ethyl group, $CH_3CH_2-$, and an $-OH$ group), $C_2H_5OH$, and $C_2H_6O$; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

**B** Taking the atomic masses from the periodic table, we obtain

$$2 \times \ atomic\ mass\ of\ carbon = 2\ \cancel{atoms}\ \frac{12.011\ amu}{\cancel{atom}} = 24.022\ amu$$

$$6 \times \ atomic\ mass\ of\ hydrogen = 6\ \cancel{atoms}\ \frac{1.0079\ amu}{\cancel{atom}} = 6.0474\ amu$$

$$1 \times \ atomic\ mass\ of\ oxygen = 1\ \cancel{atoms}\ \frac{15.994\ amu}{\cancel{atom}} = 15.994\ amu$$

**C** Adding together the masses gives the molecular mass:

24.022 amu + 6.0474 amu + 15.9994 amu = 46.069 amu

Alternatively, we could have used unit conversions to reach the result in one step, as described in Essential Skills 2 (Section 3.7):

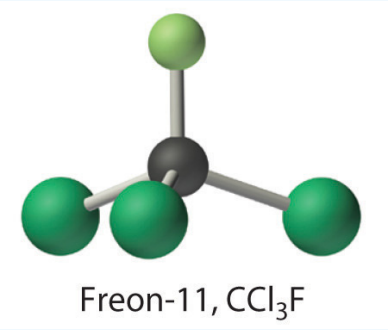
$$\left[2\ \cancel{atoms\ C}\left(\frac{12.011\ amu}{1\ \cancel{atom\ C}}\right)\right]+\left[6\ \cancel{atoms\ H}\left(\frac{1.0079\ amu}{1\ \cancel{atom\ H}}\right)\right]$$
$$+\left[1\ \cancel{atoms\ O}\left(\frac{15.994\ amu}{1\ \cancel{atom\ C}}\right)\right]=46.069$$

The same calculation can also be done in a tabular format, which is especially helpful for more complex molecules:

| Atoms | Atomic weights |
|---|---|
| 2C | (2 atoms)(12.011 amu/atom) = 24.022 amu |
| 6H | (6 atoms)(1.0079 amu/atom) = 6.0474 amu |
| 1O | (1 atoms)(15.9994 amu/atom) = 15.9994 amu |
| $C_2H_6O$ | molecular mass of ethanol = 46.069 amu |

## ? Exercise 3.1.1

Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, whose condensed structural formula is $CCl_3F$. Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:




**Answer**

137.368 amu

Unlike molecules, which have covalent bonds, ionic compounds do not have a readily identifiable molecular unit. So for ionic compounds we use the *formula mass* (also called the **empirical formula mass**) of the compound rather than the molecular mass. The **formula mass** is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. Once again, the units are atomic mass units.

### Note the Pattern

Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.

## ✓ Example 3.1.2

Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

**Given:** ionic compound

**Asked for:** formula mass

**Strategy:**

**A** Determine the number of atoms of each element in the empirical formula.

**B** Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

**C** Add together the masses to give the formula mass.

**Solution**

**A** The empirical formula—$Ca_3(PO_4)_2$—indicates that the simplest electrically neutral unit of calcium phosphate contains three $Ca^{2+}$ ions and two $PO_4^{3-}$ ions. The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.

**B** Taking atomic masses from the periodic table, we obtain

$$atomic\ mass\ of\ calcium = 3\ \cancel{atoms}\left(\frac{40.078\ amu}{\cancel{atom}}\right) = 120.234\ amu$$

$$atomic\ mass\ of\ phosphorus = 2\ \cancel{atoms}\left(\frac{30.973761\ amu}{\cancel{atom}}\right) = 61.947522\ amu$$

$$atomic\ mass\ of\ oxygen = 8\ \cancel{atoms}\left(\frac{15.9994\ amu}{\cancel{atom}}\right) = 127.9952\ amu$$

**C** Adding together the masses gives the formula mass of $Ca_3(PO_4)_2$:

$$120.234\ amu + 61.947522\ amu + 127.9952\ amu = 310.177\ amu \tag{3.1.1}$$

We could also find the formula mass of $Ca_3(PO_4)_2$ in one step by using unit conversions or a tabular format:

$$\left[3\ atoms\ Ca\left(\frac{40.078\ amu}{1\ atom\ Ca}\right)\right] + \left[2\ atoms\ P\left(\frac{30.973761\ amu}{1\ atom\ P}\right)\right] + \left[8\ atoms\ O\left(\frac{15.9994\ amu}{1\ atom\ O}\right)\right] = 310.177\ amu$$

| Atoms | Atomic weights |
|---|---|
| 3Ca | (3 atoms)(40.078 amu/atom) = 24.022 amu |
| 2P | (2 atoms)(30.973761 amu/atom) = 6.0474 amu |
| 8O | (8 atoms)(15.9994 amu/atom) = 127.9952 amu |
| $Ca_3P_2O_8$ | formula mass of $Ca_3(PO_4)_2$ = 310.177 amu |

**? Exercise 3.1.2**

Calculate the formula mass of $Si_3N_4$, commonly called silicon nitride. It is an extremely hard and inert material that is used to make cutting tools for machining hard metal alloys.

**Answer**

140.29 amu

## The Mole

In Chapter 1, we described Dalton's theory that each chemical compound has a particular combination of atoms and that the ratios of the *numbers* of atoms of the elements present are usually small whole numbers. We also described the **law of multiple proportions**, which states that the ratios of the *masses* of elements that form a series of compounds are small whole numbers. The problem for Dalton and other early chemists was to discover the quantitative relationship between the number of atoms in a

chemical substance and its mass. Because the masses of individual atoms are so minuscule (on the order of $10^{-23}$ g/atom), chemists do not measure the mass of individual atoms or molecules. In the laboratory, for example, the masses of compounds and elements used by chemists typically range from milligrams to grams, while in industry, chemicals are bought and sold in kilograms and tons. To analyze the transformations that occur between individual atoms or molecules in a **chemical reaction**, it is therefore absolutely essential for chemists to know how many atoms or molecules are contained in a measurable quantity in the laboratory—a given mass of sample. The unit that provides this link is the **mole (mol)**, from the Latin *moles*, meaning "pile" or "heap" (*not* from the small subterranean animal!).

Many familiar items are sold in numerical quantities that have unusual names. For example, cans of soda come in a six-pack, eggs are sold by the dozen (12), and pencils often come in a gross (12 dozen, or 144). Sheets of printer paper are packaged in reams of 500, a seemingly large number. Atoms are so small, however, that even 500 atoms are too small to see or measure by most common techniques. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extraordinarily large numerical unit is needed to count them. The mole is used for this purpose.

A **mole** is defined as the amount of a substance that contains the number of carbon atoms in exactly 12 g of isotopically pure carbon-12. According to the most recent experimental measurements, this mass of carbon-12 contains $6.022142 \times 10^{23}$ atoms, but for most purposes $6.022 \times 10^{23}$ provides an adequate number of significant figures. Just as 1 mol of atoms contains $6.022 \times 10^{23}$ atoms, 1 mol of eggs contains $6.022 \times 10^{23}$ eggs. The number in a mole is called **Avogadro's number**, after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain.

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that *1 mol of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: $6.022 \times 10^{23}$.*

### Note the Pattern

One mole always has the same number of objects: $6.022 \times 10^{23}$.

To appreciate the magnitude of Avogadro's number, consider a mole of pennies. Stacked vertically, a mole of pennies would be $4.5 \times 10^{17}$ mi high, or almost six times the diameter of the Milky Way galaxy. If a mole of pennies were distributed equally among the entire population on Earth, each person would get more than one trillion dollars. Clearly, the mole is so large that it is useful only for measuring very small objects, such as atoms.

The concept of the mole allows us to count a specific number of individual atoms and molecules by weighing measurable quantities of elements and compounds. To obtain 1 mol of carbon-12 atoms, we would weigh out 12 g of isotopically pure carbon-12. Because each element has a different atomic mass, however, a mole of each element has a different mass, even though it contains the same number of atoms ($6.022 \times 10^{23}$). This is analogous to the fact that a dozen extra large eggs weighs more than a dozen small eggs, or that the total weight of 50 adult humans is greater than the total weight of 50 children. Because of the way in which the mole is defined, for every element the number of grams in a mole is the same as the number of atomic mass units in the atomic mass of the element. For example, the mass of 1 mol of magnesium (atomic mass = 24.305 amu) is 24.305 g. Because the atomic mass of magnesium (24.305 amu) is slightly more than twice that of a carbon-12 atom (12 amu), the mass of 1 mol of magnesium atoms (24.305 g) is slightly more than twice that of 1 mol of carbon-12 (12 g). Similarly, the mass of 1 mol of helium (atomic mass = 4.002602 amu) is 4.002602 g, which is about one-third that of 1 mol of carbon-12. Using the concept of the mole, we can now restate Dalton's theory: *1 mol of a compound is formed by combining elements in amounts whose mole ratios are small whole numbers.* For example, 1 mol of water ($H_2O$) has 2 mol of hydrogen atoms and 1 mol of oxygen atoms.

## Molar Mass

The **molar mass** of a substance is defined as the mass in grams of 1 mol of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element; for a covalent molecular compound, it is the mass of 1 mol of molecules of that compound; for an ionic compound, it is the mass of 1 mol of formula units. That is, the molar mass of a substance is the mass (in grams per mole) of $6.022 \times 10^{23}$ atoms, molecules, or formula units of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

### Note the Pattern

The molar mass of any substance is its atomic mass, molecular mass, or formula mass in grams per mole.

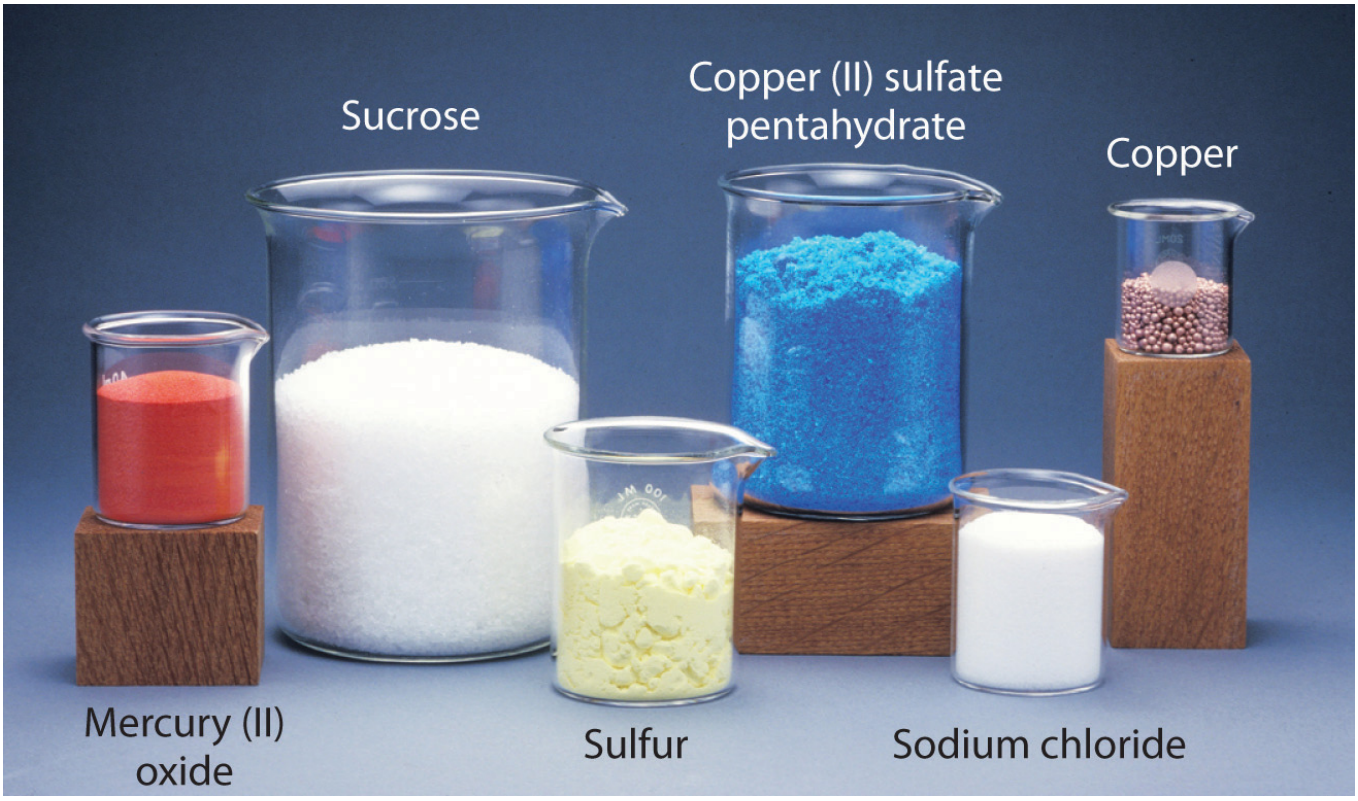
The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of $6.022 \times 10^{23}$ carbon atoms—is therefore 12.011 g/mol:

| Substance (formula) | Atomic, Molecular, or Formula Mass (amu) | Molar Mass (g/mol) |
|---|---|---|
| carbon (C) | 12.011 (atomic mass) | 12.011 |
| ethanol ($C_2H_5OH$) | 46.069 (molecular mass) | 46.069 |
| calcium phosphate [$Ca_3(PO_4)_2$] | 310.177 (formula mass) | 310.177 |

The molar mass of naturally occurring carbon is different from that of carbon-12 and is not an integer because carbon occurs as a mixture of carbon-12, carbon-13, and carbon-14. One mole of carbon still has $6.022 \times 10^{23}$ carbon atoms, but 98.89% of those atoms are carbon-12, 1.11% are carbon-13, and a trace (about 1 atom in $10^{12}$) are carbon-14. (For more information, see Section 1.7.) Similarly, the molar mass of uranium is 238.03 g/mol, and the molar mass of iodine is 126.90 g/mol. When we deal with elements such as iodine and sulfur, which occur as a diatomic molecule ($I_2$) and a polyatomic molecule ($S_8$), respectively, molar mass usually refers to the mass of 1 mol of *atoms* of the element—in this case I and S, *not* to the mass of 1 mol of *molecules* of the element ($I_2$ and $S_8$).

The molar mass of ethanol is the mass of ethanol ($C_2H_5OH$) that contains $6.022 \times 10^{23}$ ethanol molecules. As you calculated in Example 1, the molecular mass of ethanol is 46.069 amu. Because 1 mol of ethanol contains 2 mol of carbon atoms ($2 \times 12.011$ g), 6 mol of hydrogen atoms ($6 \times 1.0079$ g), and 1 mol of oxygen atoms ($1 \times 15.9994$ g), its molar mass is 46.069 g/mol. Similarly, the formula mass of calcium phosphate [$Ca_3(PO_4)_2$] is 310.177 amu, so its molar mass is 310.177 g/mol. This is the mass of calcium phosphate that contains $6.022 \times 10^{23}$ formula units. Figure 3.1.1 shows samples that contain precisely one molar mass of several common substances.

Figure 3.1.1 *Samples of 1 Mol of Some Common Substances (CC-BY-SA-NC-4.0 Los cambios químicos, Marta Espina Fernández)*



The mole is the basis of quantitative chemistry. It provides chemists with a way to convert easily between the mass of a substance and the number of individual atoms, molecules, or formula units of that substance. Conversely, it enables chemists to calculate the mass of a substance needed to obtain a desired number of atoms, molecules, or formula units. For example, to convert moles of a substance to mass, we use the relationship

$$(moles)(molar\ mass) \rightarrow mass \tag{7.1.1}$$

or, more specifically,

$$\cancel{moles}\left(\frac{grams}{\cancel{mole}}\right) = grams$$

Conversely, to convert the mass of a substance to moles, we use

$$moles\left(\frac{grams}{mole}\right) = grams$$

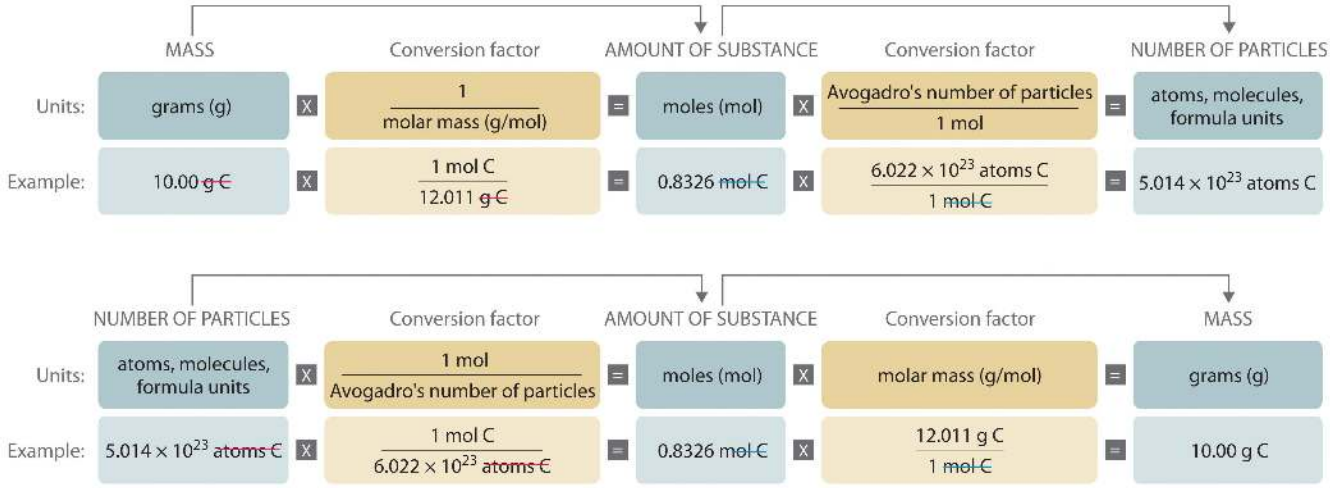
$$\left(\frac{mass}{molar\ mass}\right) \rightarrow moles$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles$$

Be sure to pay attention to the units when converting between mass and moles.

Figure 3.1.2 is a flowchart for converting between mass; the number of moles; and the number of atoms, molecules, or formula units. The use of these conversions is illustrated in Example 3 and Example 4.

Figure 3.1.2 *A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units*




## Example 3.1.3

For 35.00 g of ethylene glycol ($HOCH_2CH_2OH$), which is used in inks for ballpoint pens, calculate the number of

1. moles.
2. molecules.

**Given:** mass and molecular formula

**Asked for:** number of moles and number of molecules

**Strategy:**

**A** Use the molecular formula of the compound to calculate its molecular mass in grams per mole.

**B** Convert from mass to moles by dividing the mass given by the compound's molar mass.

**C** Convert from moles to molecules by multiplying the number of moles by Avogadro's number.

**Solution**

1. **A** The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 1:

$$\begin{array}{rll} 2\text{C} & (2 \text{ atoms})(12.011\text{amu/ atom}) & = 24.022\text{amu} \\ 6\text{H} & (6 \text{ atoms})(1.0079\text{amu/ atom}) & = 6.0474\text{amu} \\ +2\text{O} & (2 \text{ atoms})(15.9994\text{amu/ atom}) & = 31.9988\text{amu} \\ \hline \text{C}_2\text{H}_6\text{O}_2 & \text{molecular mass of ethylene glycol} & = 62.068\text{amu} \end{array} \tag{3.1.2}$$

| Atoms | Atomic weights |
|---|---|
| 2C | (2 atoms)(12.011 amu/atom) = 24.022 amu |
| 6H | (6 atoms)(1.0079 amu/atom) = 6.0474 amu |
| 2O | (2 atoms)(15.9994 amu/atom) = 31.9988 amu |
| C2H6O | molecular mass of ethanol = 62.068 amu |

The molar mass of ethylene glycol is 62.068 g/mol.

2. **B** The number of moles of ethylene glycol present in 35.00 g can be calculated by dividing the mass (in grams) by the molar mass (in grams per mole):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)} \tag{3.1.3}$$

So

$$\begin{aligned} &35.00 \text{ g ethylene glycol} \left( \frac{1 \text{ mol ethylene glycol}}{62.068 \text{ g ethylene glycol}} \right) \\ &= 0.5639 \text{ mol ethylene glycol} \end{aligned} \tag{3.1.4}$$

*It is always a good idea to estimate the answer before you do the actual calculation*. In this case, the mass given (35.00 g) is *less* than the molar mass, so the answer should be less than 1 mol. The calculated answer (0.5639 mol) is indeed less than 1 mol, so we have probably not made a major error in the calculations.

3. **C** To calculate the number of molecules in the sample, we multiply the number of moles by Avogadro's number:

$$\begin{aligned} &\text{molecules of ethylene glycol } = 0.5639 \text{ mol} \left( \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) \\ &= 3.396 \times 10^{23} \text{ molecules} \end{aligned} \tag{3.1.5}$$

Because we are dealing with slightly more than 0.5 mol of ethylene glycol, we expect the number of molecules present to be slightly more than one-half of Avogadro's number, or slightly more than $3 \times 10^{23}$ molecules, which is indeed the case.

## ? Exercise 3.1.3

For 75.0 g of $CCl_3F$ (Freon-11), calculate the number of

1. moles.
2. molecules.

**Answer**

a. 0.546 mol

b. $3.29 \times 10^{23}$ molecules

## Example 3.1.4

Calculate the mass of 1.75 mol of each compound.

1. $S_2Cl_2$ (common name: sulfur monochloride; systematic name: disulfur dichloride)
2. $Ca(ClO)_2$ (calcium hypochlorite)

**Given:** number of moles and molecular or empirical formula

**Asked for:** mass

**Strategy:**

**A** Calculate the molecular mass of the compound in grams from its molecular formula (if covalent) or empirical formula (if ionic).

**B** Convert from moles to mass by multiplying the moles of the compound given by its molar mass.

**Solution**

We begin by calculating the molecular mass of $S_2Cl_2$ and the formula mass of $Ca(ClO)_2$.

**A** The molar mass of $S_2Cl_2$ is obtained from its molecular mass as follows:

| Atoms | Atomic weights |
|---|---|
| 2S | (2 atoms)(32.065 amu/atom) = 64.130 amu |
| 2Cl | (2 atoms)(35.353 amu/atom) = 70.906 amu |
| $S_2Cl_2$ | molecular mass of $S_2Cl_2$ = 135.036 amu |

The molar mass of $S_2Cl_2$ is 135.036 g/mol.

**B** The mass of 1.75 mol of $S_2Cl_2$ is calculated as follows:

$$moles\ S_2Cl_2 \left[molar\ mass \frac{g}{mol}\right] = mass\ S_2Cl_2$$

$$1.75\ mol\ S_2Cl_2 \left(\frac{135.036\ g\ S_2Cl_2}{1\ mol\ S_2Cl_2}\right) = 236\ g\ S_2Cl_2$$

**A** The formula mass of $Ca(ClO)_2$ is obtained as follows:

| Atoms | Atomic weights |
|---|---|
| 1Ca | (1 atom )(40.078 amu/atom) = 40.078 amu |
| 2Cl | (2 atoms)(35.453 amu/atom) = 70.906 amu |
| 2O | (2 atoms)(15.9994 amu/atom) = 31.9988 amu |
| $Ca(ClO)_2$ | **formula** mass of $Ca(ClO)_2$ = 142.983 amu |

The molar mass of $Ca(ClO)_2$ 142.983 g/mol.

**B** The mass of 1.75 mol of $Ca(ClO)_2$ is calculated as follows:

$$moles\ Ca\,(ClO)_2 \left[\frac{molar\ mass\ Ca\,(ClO)_2}{1\ mol\ Ca\,(ClO)_2}\right] = mass\ Ca\,(ClO)_2$$

$$1.75\ mol\ Ca\,(ClO)_2 \left[\frac{142.983\ gCa\,(ClO)_2}{1\ mol\ Ca\,(ClO)_2}\right] = 250.\ g\ Ca\,(ClO)_2$$

Because 1.75 mol is less than 2 mol, the final quantity in grams in both cases should be less than twice the molar mass, which it is.

**? Exercise 3.1.4**

Calculate the mass of 0.0122 mol of each compound.

1. $Si_3N_4$ (silicon nitride), used as bearings and rollers
2. $(CH_3)_3N$ (trimethylamine), a corrosion inhibitor

**Answer**

1. 1.71 g
2. 0.721 g

## Summary

The **molecular mass** and the **formula mass** of a compound are obtained by adding together the atomic masses of the atoms present in the molecular formula or empirical formula, respectively; the units of both are atomic mass units (amu). The **mole** is a unit used to measure the number of atoms, molecules, or (in the case of ionic compounds) formula units in a given mass of a substance. The mole is defined as the amount of substance that contains the number of carbon atoms in exactly 12 g of carbon-12 and consists of **Avogadro's number** ($6.022 \times 10^{23}$) of atoms of carbon-12. The **molar mass** of a substance is defined as the mass of 1 mol of that substance, expressed in grams per mole, and is equal to the mass of $6.022 \times 10^{23}$ atoms, molecules, or formula units of that substance.

## KEY TAKEAWAY

- To analyze chemical transformations, it is essential to use a standardized unit of measure called the mole.

## CONCEPTUAL PROBLEMS

*Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7) before proceeding to the Conceptual Problems.*

1. Describe the relationship between an atomic mass unit and a gram.
2. Is it correct to say that ethanol has a formula mass of 46? Why or why not?
3. If 2 mol of sodium react completely with 1 mol of chlorine to produce sodium chloride, does this mean that 2 g of sodium reacts completely with 1 g of chlorine to give the same product? Explain your answer.
4. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain.
5. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

## Answer

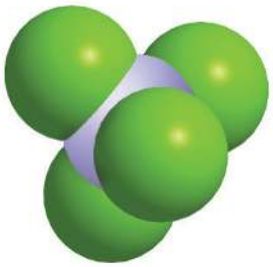
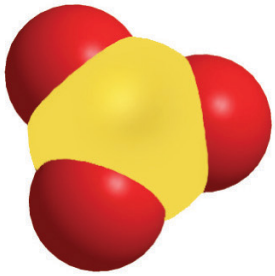
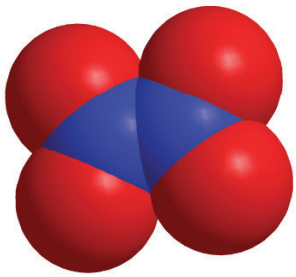
1.
2.
3.
4.
5. A = %N by mass, expressed as a decimal

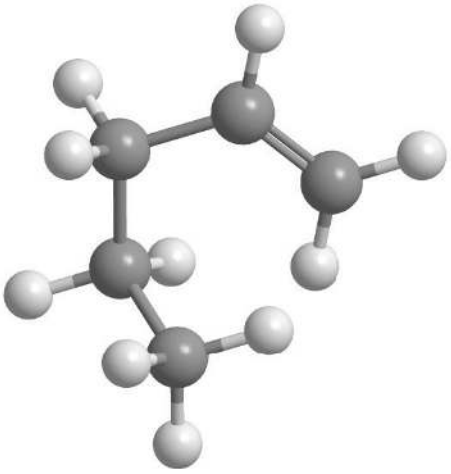
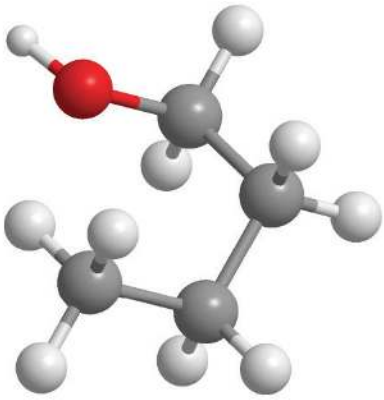
   B =1molar mass of nitrogen in g

   g nitroglycerin$-\!\!\rightarrow \times$AgN$-\!\!\rightarrow \times$Bmol N

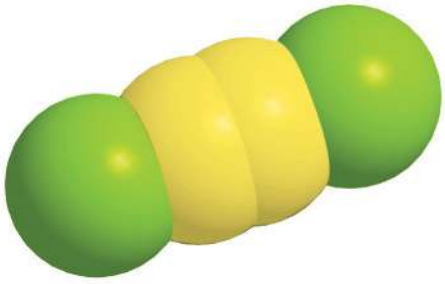
## NUMERICAL PROBLEMS

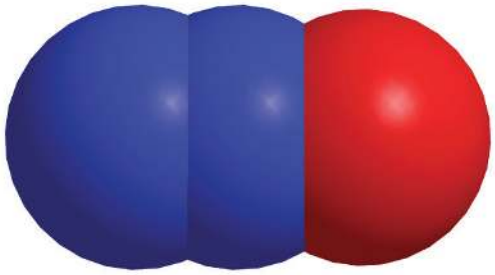
*Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7) before proceeding to the Numerical Problems.*

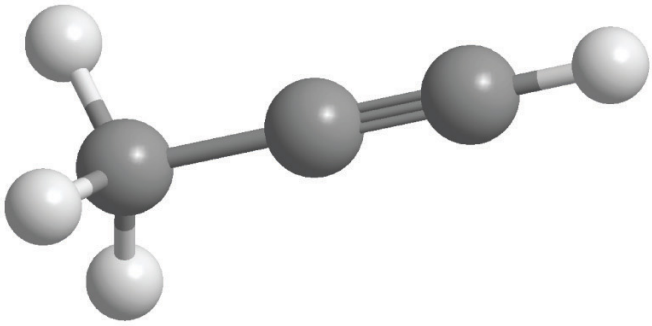
1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.
2. Calculate the molecular mass or formula mass of each compound.
    1. KCl (potassium chloride)
    2. NaCN (sodium cyanide)
    3. $H_2S$ (hydrogen sulfide)
    4. $NaN_3$ (sodium azide)
    5. $H_2CO_3$ (carbonic acid)
    6. $K_2O$ (potassium oxide)
    7. $Al(NO_3)_3$ (aluminum nitrate)
    8. $Cu(ClO_4)_2$ [copper(II) perchlorate]
3. Calculate the molecular mass or formula mass of each compound.
    1. $V_2O_4$ (vanadium(IV) oxide)
    2. $CaSiO_3$ (calcium silicate)
    3. BiOCl (bismuth oxychloride)
    4. $CH_3COOH$ (acetic acid)
    5. $Ag_2SO_4$ (silver sulfate)
    6. $Na_2CO_3$ (sodium carbonate)
    7. $(CH_3)_2CHOH$ (isopropyl alcohol)
4. Calculate the molar mass of each compound.
    1. 
    2. 
    3. 

4. 
5. 

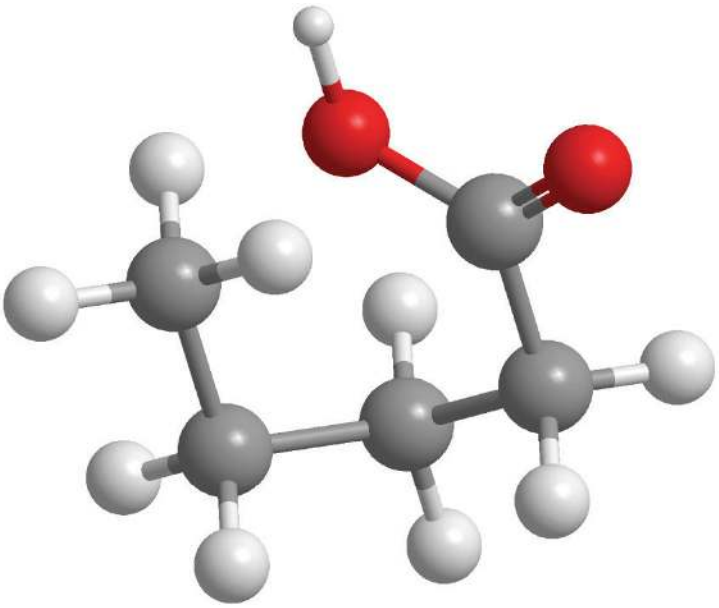
5. Calculate the molar mass of each compound.

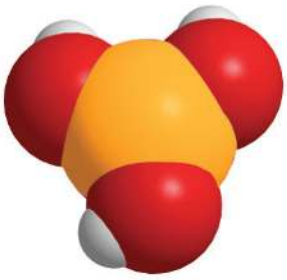
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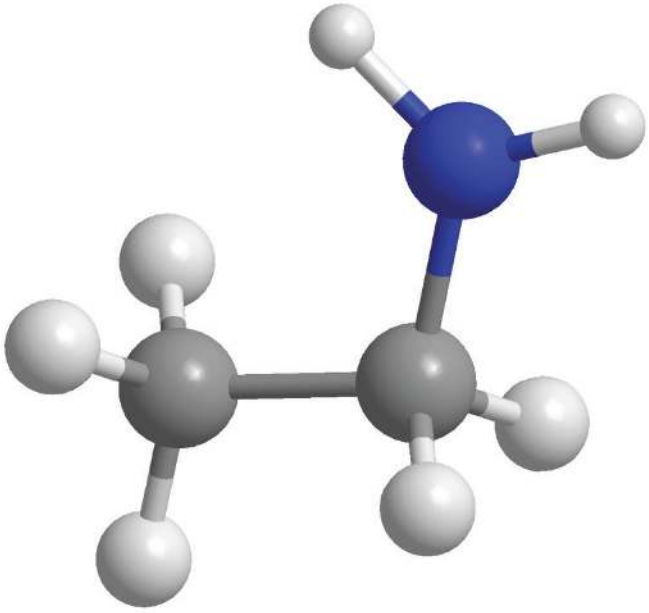
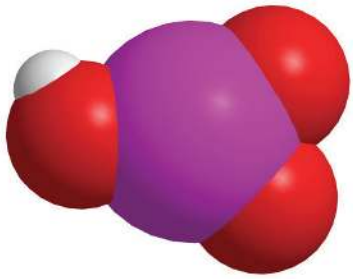
4. 

6. For each compound, write the condensed formula, name the compound, and give its molar mass.

1. 

2. 

7. For each compound, write the condensed formula, name the compound, and give its molar mass.

1. 
2. 

8. Calculate the number of moles in $5.00 \times 10^2$ g of each substance. How many molecules or formula units are present in each sample?
    1. CaO (lime)
    2. $CaCO_3$ (chalk)
    3. $C_{12}H_{22}O_{11}$ [sucrose (cane sugar)]
    4. NaOCl (bleach)
    5. $CO_2$ (dry ice)
9. Calculate the mass in grams of each sample.
    1. 0.520 mol of $N_2O_4$
    2. 1.63 mol of $C_6H_4Br_2$
    3. 4.62 mol of $(NH_4)_2SO_3$
10. Give the number of molecules or formula units in each sample.
    1. $1.30 \times 10^{-2}$ mol of $SCl_2$
    2. 1.03 mol of $N_2O_5$
    3. 0.265 mol of $Ag_2Cr_2O_7$
11. Give the number of moles in each sample.
    1. $9.58 \times 10^{26}$ molecules of $Cl_2$
    2. $3.62 \times 10^{27}$ formula units of KCl
    3. $6.94 \times 10^{28}$ formula units of $Fe(OH)_2$
12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine ($I_2$)?
13. What is the total number of atoms in each sample?

1. 0.431 mol of Li
2. 2.783 mol of methanol ($CH_3OH$)
3. 0.0361 mol of $CoCO_3$
4. 1.002 mol of $SeBr_2O$

14. What is the total number of atoms in each sample?
    1. 0.980 mol of Na
    2. 2.35 mol of $O_2$
    3. 1.83 mol of $Ag_2S$
    4. 1.23 mol of propane ($C_3H_8$)
15. What is the total number of atoms in each sample?
    1. 2.48 g of HBr
    2. 4.77 g of $CS_2$
    3. 1.89 g of NaOH
    4. 1.46 g of $SrC_2O_4$
16. Decide whether each statement is true or false and explain your reasoning.
    1. There are more molecules in 0.5 mol of $Cl_2$ than in 0.5 mol of $H_2$.
    2. One mole of $H_2$ has $6.022 \times 10^{23}$ hydrogen atoms.
    3. The molecular mass of $H_2O$ is 18.0 amu.
    4. The formula mass of benzene is 78 amu.
17. Complete the following table.

| Substance | Mass (g) | Number of Moles | Number of Molecules or Formula Units | Number of Atoms or Ions |
|---|---|---|---|---|
| $MgCl_2$ | 37.62 | | | |
| $AgNO_3$ | | 2.84 | | |
| $BH_4Cl$ | | | $8.93 \times 10^{25}$ | |
| $K_2S$ | | | | $7.69 \times 10^{26}$ |
| $H_2SO_4$ | | 1.29 | | |
| $C_6H_{14}$ | 11.84 | | | |
| $HClO_3$ | | | $2.45 \times 10^{26}$ | |

18. Give the formula mass or the molecular mass of each substance.
    1. PbClF
    2. $Cu_2P_2O_7$
    3. $BiONO_3$
    4. $Tl_2SeO_4$
19. Give the formula mass or the molecular mass of each substance.
    1. $MoCl_5$
    2. $B_2O_3$
    3. $UO_2CO_3$
    4. $NH_4UO_2AsO_4$

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# 3.2: Determining Empirical and Molecular Formulas

**Learning Objectives**

- To determine the empirical formula of a compound from its composition by mass.
- To derive the molecular formula of a compound from its empirical formula.

When a new chemical compound, such as a potential new pharmaceutical, is synthesized in the laboratory or isolated from a natural source, chemists determine its elemental composition, its empirical formula, and its structure to understand its properties. In this section, we focus on how to determine the empirical formula of a compound and then use it to determine the molecular formula if the molar mass of the compound is known.

## Calculating Mass Percentages

The law of definite proportions states that a chemical compound always contains the same proportion of elements by mass; that is, the percent composition (the percentage of each element present in a pure substance). With few exceptions, the percent composition of a chemical compound is constant (see law of definite proportions).—the percentage of each element present in a pure substance —is constant (although we now know there are exceptions to this law). For example, sucrose (cane sugar) is 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. This means that 100.00 g of sucrose always contains 42.11 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen. First we will use the molecular formula of sucrose ($C_{12}H_{22}O_{11}$) to calculate the mass percentage of the component elements; then we will show how mass percentages can be used to determine an empirical formula.

According to its molecular formula, each molecule of sucrose contains 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. A mole of sucrose molecules therefore contains 12 mol of carbon atoms, 22 mol of hydrogen atoms, and 11 mol of oxygen atoms. We can use this information to calculate the mass of each element in 1 mol of sucrose, which will give us the molar mass of sucrose. We can then use these masses to calculate the percent composition of sucrose. To three decimal places, the calculations are the following:

$$mass\ of\ C/mol\ of\ sucrose = 12\ \cancel{mol}\left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}}\right) = 144.132\ g\ C$$

$$mass\ of\ H/mol\ of\ sucrose = 22\ \cancel{mol}\left(\frac{1.008\ g\ H}{1\ \cancel{mol\ H}}\right) = 22.176\ g\ H\ )$$

$$mass\ of\ O/mol\ of\ sucrose = 11\ \cancel{mol}\left(\frac{15.999\ g\ O}{1\ \cancel{mol\ O}}\right) = 175.989\ g\ O$$

Thus 1 mol of sucrose has a mass of 342.297 g; note that more than half of the mass (175.989 g) is oxygen, and almost half of the mass (144.132 g) is carbon.

The mass percentage of each element in sucrose is the mass of the element present in 1 mol of sucrose divided by the molar mass of sucrose, multiplied by 100 to give a percentage. The result is shown to two decimal places:

$$mass\ \%\ C\ in\ sucrose = \frac{mass\ of\ C/mol\ sucrose}{molar\ mass\ of\ sucrose} \times 100 = \frac{144.132\ g\ C}{342.297\ g/mol} \times 100 = 42.12\%$$

$$mass\ \%\ H\ in\ sucrose = \frac{mass\ of\ H/mol\ sucrose}{molar\ mass\ of\ sucrose} \times 100 = \frac{22.176\ g\ H}{342.297\ g/mol} \times 100 = 6.48\%$$

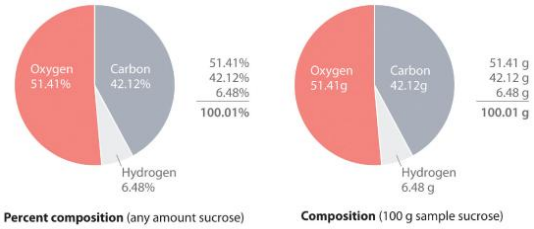
$$mass\ \%\ O\ in\ sucrose = \frac{mass\ of\ O/mol\ sucrose}{molar\ mass\ of\ sucrose} \times 100 = \frac{175.989\ g\ O}{342.297\ g/mol} \times 100 = 51.41\%$$

You can check your work by verifying that the sum of the percentages of all the elements in the compound is 100%:

$$42.12\% + 6.48\% + 51.41\% = 100.01\%$$

If the sum is not 100%, you have made an error in your calculations. (Rounding to the correct number of decimal places can, however, cause the total to be slightly different from 100%.) Thus 100.00 g of sucrose contains 42.12 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen; to two decimal places, the percent composition of sucrose is indeed 42.12% carbon, 6.48% hydrogen, and 51.41% oxygen.

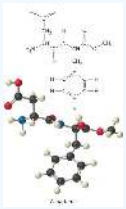
**Figure** 3.2.1 ***Percent Composition***




We could also calculate the mass percentages using atomic masses and molecular masses, with atomic mass units. Because the answer we are seeking is a ratio, expressed as a percentage, the units of mass cancel whether they are grams (using molar masses) or atomic mass units (using atomic and molecular masses).

## Example 3.2.1

Aspartame is the artificial sweetener sold as NutraSweet and Equal. Its molecular formula is $C_{14}H_{18}N_2O_5$.



1. Calculate the mass percentage of each element in aspartame.
2. Calculate the mass of carbon in a 1.00 g packet of Equal, assuming it is pure aspartame.

**Given:** molecular formula and mass of sample

**Asked for:** mass percentage of all elements and mass of one element in sample

**Strategy:**

**A** Use atomic masses from the periodic table to calculate the molar mass of aspartame.

**B** Divide the mass of each element by the molar mass of aspartame; then multiply by 100 to obtain percentages.

**C** To find the mass of an element contained in a given mass of aspartame, multiply the mass of aspartame by the mass percentage of that element, expressed as a decimal.

**Solution**

1. **A** We calculate the mass of each element in 1 mol of aspartame and the molar mass of aspartame, here to three decimal places:

| Atoms | # atoms x atomic weight | Result |
|---|---|---|
| 14 C | (14 mol C)(12.011 g/mol C) = | 168.154 g |
| 18 H | (18 mol H)(1.008 g/mol H) = | 18.114 g |
| 2N | (2 mol N)(14.007 g/mol N) = | 28.014 g |
| +5O | (5 mol O)(15.999 g/mol O) = | 79.995 g |
| $C_{14}H_{18}N_2O_5$ | molar mass of aspartame | 294.277 g/mol |

Thus more than half the mass of 1 mol of aspartame (294.277 g) is carbon (168.154 g).

**B** To calculate the mass percentage of each element, we divide the mass of each element in the compound by the molar mass of aspartame and then multiply by 100 to obtain percentages, here reported to two decimal places:

$$mass\ \%\ C = \frac{168.154\ g\ C}{294.277\ g\ aspartame} \times 100 = 57.14\%\ C$$

$$mass\ \%\ N = \frac{18.114\ g\ H}{294.277\ g\ aspartame} \times 100 = 6.16\%\ C$$

$$mass\ \%\ N = \frac{28.014\ g\ N}{294.277\ g\ aspartame} \times 100 = 9.52\%\ C$$

$$mass\ \%\ O = \frac{79.995\ g\ O}{294.277\ g\ aspartame} \times 100 = 27.18\%\ C$$

As a check, we can add the percentages together:

**57.14% + 6.16% + 9.52% + 27.18% = 100.00%**

If you obtain a total that differs from 100% by more than about ±1%, there must be an error somewhere in the calculation.

2. **C** The mass of carbon in 1.00 g of aspartame is calculated as follows: $mass\ of\ C = 1.00\ \cancel{g\ aspartame} \times \frac{57.14\ g\ C}{100\ \cancel{g\ aspartame}} = 0.57\grave{}\ g\ C$

Add text here.

**? Exercise 3.2.1**

Calculate the mass percentage of each element in aluminum oxide ($Al_2O_3$). Then calculate the mass of aluminum in a 3.62 g sample of pure aluminum oxide.

**Answer**

52.93% aluminum; 47.08% oxygen; 1.92 g Al

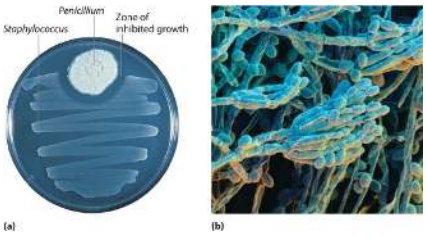
## Determining the Empirical Formula of Penicillin

Just as we can use the empirical formula of a substance to determine its percent composition, we can use the percent composition of a sample to determine its empirical formula, which can then be used to determine its molecular formula. Such a procedure was actually used to determine the empirical and molecular formulas of the first antibiotic to be discovered: penicillin.

*Antibiotics* are chemical compounds that selectively kill microorganisms, many of which cause diseases. Although we may take antibiotics for granted today, penicillin was discovered only about 80 years ago. The subsequent development of a wide array of other antibiotics for treating many common diseases has contributed greatly to the substantial increase in life expectancy over the past 50 years. The discovery of penicillin is a historical detective story in which the use of mass percentages to determine empirical formulas played a key role.

In 1928, Alexander Fleming, a young microbiologist at the University of London, was working with a common bacterium that causes boils and other infections such as blood poisoning. For laboratory study, bacteria are commonly grown on the surface of a nutrient-containing gel in small, flat culture dishes. One day Fleming noticed that one of his cultures was contaminated by a bluish-green mold similar to the mold found on spoiled bread or fruit. Such accidents are rather common, and most laboratory workers would have simply thrown the cultures away. Fleming noticed, however, that the bacteria were growing everywhere on the gel *except* near the contaminating mold (part (a) in Figure 3.2.2, and he hypothesized that the mold must be producing a substance that either killed the bacteria or prevented their growth. To test this hypothesis, he grew the mold in a liquid and then filtered the liquid and added it to various bacteria cultures. The liquid killed not only the bacteria Fleming had originally been studying but also a wide range of other disease-causing bacteria. Because the mold was a member of the *Penicillium* family (named for their pencil-shaped branches under the microscope) (part (b) in Figure 3.2.2), Fleming called the active ingredient in the broth *penicillin*.

Figure 3.2.2 ***Penicillium***




*(a) Penicillium mold is growing in a culture dish; the photo shows its effect on bacterial growth. (b) In this photomicrograph of Penicillium, its rod- and pencil-shaped branches are visible. The name comes from the Latin penicillus, meaning "paintbrush."*

Although Fleming was unable to isolate penicillin in pure form, the medical importance of his discovery stimulated researchers in other laboratories. Finally, in 1940, two chemists at Oxford University, Howard Florey (1898–1968) and Ernst Chain (1906–1979), were able to isolate an active product, which they called penicillin G. Within three years, penicillin G was in widespread use for treating pneumonia, gangrene, gonorrhea, and other diseases, and its use greatly increased the survival rate of wounded soldiers in World War II. As a result of their work, Fleming, Florey, and Chain shared the Nobel Prize in Medicine in 1945.

As soon as they had succeeded in isolating pure penicillin G, Florey and Chain subjected the compound to a procedure called combustion analysis (described later in this section) to determine what elements were present and in what quantities. The results of such analyses are usually reported as mass percentages. They discovered that a typical sample of penicillin G contains 53.9% carbon, 4.8% hydrogen, 7.9% nitrogen, 9.0% sulfur, and 6.5% sodium by mass. The sum of these numbers is only 82.1%, rather than 100.0%, which implies that there must be one or more additional elements. A reasonable candidate is oxygen, which is a common component of compounds that contain carbon and hydrogen;Do not assume that the "missing" mass is always due to oxygen. It could be any other element. for technical reasons, however, it is difficult to analyze for oxygen directly. If we assume that all the missing mass is due to oxygen, then penicillin G contains (100.0% − 82.1%) = 17.9% oxygen. From these mass percentages, the empirical formula and eventually the molecular formula of the compound can be determined.

To determine the empirical formula from the mass percentages of the elements in a compound such as penicillin G, we need to convert the mass percentages to relative numbers of atoms. For convenience, we assume that we are dealing with a 100.0 g sample of the compound, even though the sizes of samples used for analyses are generally much smaller, usually in milligrams. This assumption simplifies the arithmetic because a 53.9% mass percentage of carbon corresponds to 53.9 g of carbon in a 100.0 g sample of penicillin G; likewise, 4.8% hydrogen corresponds to 4.8 g of hydrogen in 100.0 g of penicillin G; and so forth for the other elements. We can then divide each mass by the molar mass of the element to determine how many moles of each element are present in the 100.0 g sample:

$$\frac{mass(g)}{molar\ mass(g/mol)} = \left(\cancel{g}\right)\left(\frac{mol}{\cancel{g}}\right) = mol$$

$$53.9\ \cancel{g\,C}\ \frac{1\ mol\ C}{12.011\ \cancel{g\,C}} = 4.49\ mol\ C$$

$$4.8\ \cancel{g\,H}\ \frac{1\ mol\ H}{1.008\ \cancel{g\,H}} = 4.49\ mol\ H$$

$$7.9\ \cancel{g\,N}\ \frac{1\ mol\ N}{14.007\ \cancel{g\,N}} = 0.56\ mol\ N$$

$$9.0\ \cancel{g\,S}\ \frac{1\ mol\ S}{32.065\ \cancel{g\,S}} = 0.28\ mol\ S$$

$$6.5\ \cancel{g\,Na}\ \frac{1\ mol\ Na}{22.990\ \cancel{g\,Na}} = 0.28\ mol\ Na$$

$$17.9\ \cancel{g\,O}\ \frac{1\ mol\ O}{15.999\ \cancel{g\,O}} = 1.12\ mol\ O$$

Thus 100.0 g of penicillin G contains 4.49 mol of carbon, 4.8 mol of hydrogen, 0.56 mol of nitrogen, 0.28 mol of sulfur, 0.28 mol of sodium, and 1.12 mol of oxygen (assuming that all the missing mass was oxygen). The number of significant figures in the numbers of moles of elements varies between two and three because some of the analytical data were reported to only two significant figures.

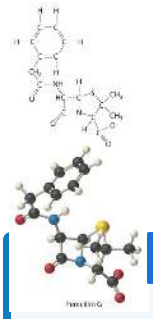
These results tell us the ratios of the moles of the various elements in the sample (4.49 mol of carbon to 4.8 mol of hydrogen to 0.56 mol of nitrogen, and so forth), but they are not the whole-number ratios we need for the empirical formula—the empirical formula expresses the *relative* numbers of atoms in the *smallest whole numbers possible*. To obtain whole numbers, we divide the numbers of moles of all the elements in the sample by the number of moles of the element present in the lowest relative amount, which in this example is sulfur or sodium. The results will be the subscripts of the elements in the empirical formula. To two significant figures, the results are

$$C: \frac{4.49}{0.28} = 16 \quad H: \frac{4.8}{0.28} = 17 \quad N: \frac{0.56}{0.28} = 2.0$$

$$S: \frac{0.28}{0.28} = 1.0 \quad Na: \frac{0.28}{0.28} = 1.0 \quad O: \frac{1.12}{0.28} = 1.0$$

The empirical formula of penicillin G is therefore $C_{16}H_{17}N_2NaO_4S$. Other experiments have shown that penicillin G is actually an ionic compound that contains $Na^+$ cations and $[C_{16}H_{17}N_2O_4S]^-$ anions in a 1:1 ratio. The complex structure of penicillin G (Figure 3.2.3) was not determined until 1948.

Figure 3.2.3 Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G



In some cases, one or more of the subscripts in a formula calculated using this procedure may not be integers. Does this mean that the compound of interest contains a nonintegral number of atoms? No; rounding errors in the calculations as well as experimental errors in the data can result in nonintegral ratios. When this happens, you must exercise some judgment in interpreting the results, as illustrated in Example 6. In particular, ratios of 1.50, 1.33, or 1.25 suggest that you should multiply *all* subscripts in the formula by 2, 3, or 4, respectively. Only if the ratio is within 5% of an integral value should you consider rounding to the nearest integer.

### ✔ Example 3.2.2

Calculate the empirical formula of the ionic compound calcium phosphate, a major component of fertilizer and a polishing agent in toothpastes. Elemental analysis indicates that it contains 38.77% calcium, 19.97% phosphorus, and 41.27% oxygen.

**Given:** percent composition

**Asked for:** empirical formula

**Strategy:**

**A** Assume a 100 g sample and calculate the number of moles of each element in that sample.

**B** Obtain the relative numbers of atoms of each element in the compound by dividing the number of moles of each element in the 100 g sample by the number of moles of the element present in the smallest amount.

**C** If the ratios are not integers, multiply all subscripts by the same number to give integral values.

**D** Because this is an ionic compound, identify the anion and cation and write the formula so that the charges balance.

**Solution**

**A** A 100 g sample of calcium phosphate contains 38.77 g of calcium, 19.97 g of phosphorus, and 41.27 g of oxygen. Dividing the mass of each element in the 100 g sample by its molar mass gives the number of moles of each element in the sample:

$$moles\ Ca = 38.77\ \cancel{g\ Ca}\ \frac{1\ mol\ Ca}{40.078\ \cancel{g\ Ca}} = 0.9674\ mol\ Ca$$

$$moles\ P = 19.97\ \cancel{g\ P}\ \frac{1\ mol\ P}{30.9738\ \cancel{g\ Ca}} = 0.6447\ mol\ P$$

$$moles\ O = 41.27\ \cancel{g\ O}\ \frac{1\ mol\ O}{15.994\ \cancel{g\ O}} = 2.5800\ mol\ O$$

**B** To obtain the *relative* numbers of atoms of each element in the compound, divide the number of moles of each element in the 100-g sample by the number of moles of the element in the smallest amount, in this case phosphorus:

$$P: \frac{0.6447\ mol P}{0.6447\ mol P} = 1.00 \quad Ca: \frac{0.9674}{0.6447} = 1.501 \quad O: \frac{2.5800}{0.6447} = 4.002$$

**C** We could write the empirical formula of calcium phosphate as $Ca_{1.501}P_{1.000}O_{4.002}$, but the empirical formula should show the ratios of the elements as small whole numbers. To convert the result to integral form, multiply all the subscripts by 2 to get $Ca_{3.002}P_{2.000}O_{8.004}$. The deviation from integral atomic ratios is small and can be attributed to minor experimental errors; therefore, the empirical formula is $Ca_3P_2O_8$.

**D** The calcium ion ($Ca^{2+}$) is a cation, so to maintain electrical neutrality, phosphorus and oxygen must form a polyatomic anion. We know from Section 6.3 2 that phosphorus and oxygen form the phosphate ion ($PO_4^{3-}$; see Table 7.21). Because there are two phosphorus atoms in the empirical formula, two phosphate ions must be present. So we write the formula of calcium phosphate as $Ca_3(PO_4)_2$.

## ? Exercise 3.2.2

Calculate the empirical formula of ammonium nitrate, an ionic compound that contains 35.00% nitrogen, 5.04% hydrogen, and 59.96% oxygen by mass; refer to Table 7.2.1 if necessary. Although ammonium nitrate is widely used as a fertilizer, it can be dangerously explosive. For example, it was a major component of the explosive used in the 1995 Oklahoma City bombing.

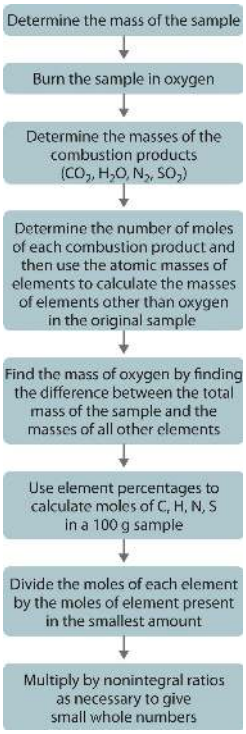
**Answer**

$N_2H_4O_3$ is $NH_4^+NO_3^-$, written as $NH_4NO_3$

## Combustion Analysis

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called *combustion analysis*. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products ($CO_2$, $H_2O$, $N_2$, and $SO_2$, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 3.2.4, and a typical combustion analysis is illustrated in Example 7.

**Figure 3.2.4 Steps for Obtaining an Empirical Formula from Combustion Analysis**




## Example 3.2.1

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of $CO_2$ and 11.30 mg of $H_2O$. Determine the empirical formula of naphthalene.

**Given:** mass of sample and mass of combustion products

**Asked for:** empirical formula

**Strategy:**

**A** Use the masses and molar masses of the combustion products, $CO_2$ and $H_2O$, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.

**B** Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

**Solution**

**A** Upon combustion, 1 mol of $CO_2$ is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of $H_2O$ is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of $CO_2$ and $H_2O$, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$mass\ of\ C = 69.00\ \cancel{mg\ CO_2} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{1\ \cancel{mol\ CO_2}}{44.010\ \cancel{g\ CO_2}} \times \frac{1\ \cancel{mol\ C}}{1\ \cancel{mol\ CO_2}} \times \frac{12.011\ g}{1\ \cancel{mol\ C}}$$

$$= 1.883 \times 10^{-2}\ g\ C)$$

$$mass\ of\ H = 11.30\ \cancel{mg\ H_2O} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{1\ \cancel{mol\ H_2O}}{18.015\ \cancel{g\ H_2O}} \times \frac{2\ \cancel{mol\ H}}{1\ \cancel{mol\ H_2O}} \times \frac{1.0079\ g}{1\ \cancel{mol\ C}}$$

$$= 1.264 \times 10^{-3}\ g\ H)$$

**B** To obtain the *relative* numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$moles\ C = 1.883 \times 10^{-2}\ \cancel{g\,C} \times \frac{1\ mol\ C}{12.011\ \cancel{g\,C}} = 1.568 \times 10^{-3}\ mol\ C$$

$$moles\ H = 1.264 \times 10^{-3}\ \cancel{g\,H} \times \frac{1\ mol\ H}{1.0079\ \cancel{g\,H}} = 1.254 \times 10^{-3}\ mol\ H$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250$$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives $C_5H_4$ as the empirical formula of naphthalene. In fact, the molecular formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

### ? Exercise 3.2.1

1. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of $CO_2$ and 14.53 mg of $H_2O$. Determine the empirical formula of xylene.
2. The empirical formula of benzene is CH (its molecular formula is $C_6H_6$). If 10.00 mg of benzene is subjected to combustion analysis, what mass of $CO_2$ and $H_2O$ will be produced?

**Answer**

1. The empirical formula is $C_4H_5$. (The molecular formula of xylene is actually $C_8H_{10}$.)
2. 33.81 mg of $CO_2$; 6.92 mg of $H_2O$

## From Empirical Formula to Molecular Formula

The empirical formula gives only the *relative* numbers of atoms in a substance in the smallest possible ratio. For a covalent substance, we are usually more interested in the molecular formula, which gives the actual number of atoms of each kind present per molecule. Without additional information, however, it is impossible to know whether the formula of penicillin G, for example, is $C_{16}H_{17}N_2NaO_4S$ or an integral multiple, such as $C_{32}H_{34}N_4Na_2O_8S_2$, $C_{48}H_{51}N_6Na_3O_{12}S_3$, or $(C_{16}H_{17}N_2NaO_4S)_n$, where $n$ is an integer. (The actual structure of penicillin G is shown in Figure 7.2.3).

Consider glucose, the sugar that circulates in our blood to provide fuel for our bodies and especially for our brains. Results from combustion analysis of glucose report that glucose contains 39.68% carbon and 6.58% hydrogen. Because combustion occurs in the presence of oxygen, it is impossible to directly determine the percentage of oxygen in a compound by using combustion analysis; other more complex methods are necessary. If we assume that the remaining percentage is due to oxygen, then glucose would contain 53.79% oxygen. A 100.0 g sample of glucose would therefore contain 39.68 g of carbon, 6.58 g of hydrogen, and 53.79 g of oxygen. To calculate the number of moles of each element in the 100.0 g sample, we divide the mass of each element by its molar mass:

$$moles\ C = 39.68\ \cancel{g\,C} \frac{1\ mol\ C}{12.011\ \cancel{g\,C}} = 3.304\ mol\ C$$

$$moles\ H = 6.58\ \cancel{g\,H} \frac{1\ mol\ H}{1.0079\ \cancel{g\,H}} = 6.53\ mol\ H$$

$$moles\ O = 53.79\ \cancel{g\,O} \frac{1\ mol\ C}{15.9994\ \cancel{g\,O}} = 3.362\ mol\ O$$

Once again, we find the subscripts of the elements in the empirical formula by dividing the number of moles of each element by the number of moles of the element present in the smallest amount:

$$C: \frac{3.304}{3.304} = 1.000 \quad H: \frac{6.53}{3.304} = 1.98 \quad O: \frac{3.362}{3.304} = 1.018$$

The oxygen:carbon ratio is 1.018, or approximately 1, and the hydrogen:carbon ratio is approximately 2. The empirical formula of glucose is therefore $CH_2O$, but what is its molecular formula?

Many known compounds have the empirical formula $CH_2O$, including formaldehyde, which is used to preserve biological specimens and has properties that are very different from the sugar circulating in our blood. At this point, we cannot know whether glucose is $CH_2O$, $C_2H_4O_2$, or any other $(CH_2O)_n$. We can, however, use the experimentally determined molar mass of glucose (180 g/mol) to resolve this dilemma.

First, we calculate the **formula mass**, the molar mass of the formula unit, which is the sum of the atomic masses of the elements in the empirical formula multiplied by their respective subscripts. For glucose,

$$formula\ mass\ of\ CH_2O = \left[1\ \cancel{mol\ C}\left(\frac{12.011\ g}{1\ \cancel{mol\ C}}\right)\right] + \left[2\ \cancel{mol\ H}\left(\frac{1.0079\ g}{1\ \cancel{mol\ H}}\right)\right] + \left[1\ \cancel{mol\ O}\left(\frac{15.9994\ g}{1\ \cancel{mol\ O}}\right)\right]$$

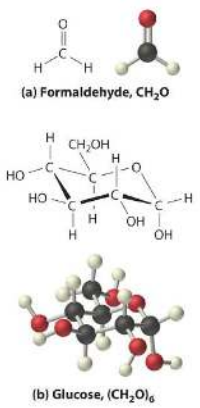
This is much smaller than the observed molar mass of 180 g/mol.

Second, we determine the number of formula units per mole. For glucose, we can calculate the number of $(CH_2O)$ units—that is, the *n* in $(CH_2O)_n$—by dividing the molar mass of glucose by the formula mass of $CH_2O$:

$$n = \frac{180\ g}{30.026\ g\ CH_2O} = 5.99 \approx 6CH^{2O}\ formula\ units$$

Each glucose contains six $CH_2O$ formula units, which gives a molecular formula for glucose of $(CH_2O)_6$, which is more commonly written as $C_6H_{12}O_6$. The molecular structures of formaldehyde and glucose, both of which have the empirical formula $CH_2O$, are shown in Figure 3.2.5

**Figure 3.2.5 Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose**




**Example 3.2.1**

Calculate the molecular formula of caffeine, a compound found in coffee, tea, and cola drinks that has a marked stimulatory effect on mammals. The chemical analysis of caffeine shows that it contains 49.18% carbon, 5.39% hydrogen, 28.65% nitrogen, and 16.68% oxygen by mass, and its experimentally determined molar mass is 196 g/mol.

**Given:** percent composition and molar mass

**Asked for:** molecular formula

**Strategy:**

**A** Assume 100 g of caffeine. From the percentages given, use the procedure given in Example 6 to calculate the empirical formula of caffeine.

**B** Calculate the formula mass and then divide the experimentally determined molar mass by the formula mass. This gives the number of formula units present.

**C** Multiply each subscript in the empirical formula by the number of formula units to give the molecular formula.

**Solution**

**A** We begin by dividing the mass of each element in 100.0 g of caffeine (49.18 g of carbon, 5.39 g of hydrogen, 28.65 g of nitrogen, 16.68 g of oxygen) by its molar mass. This gives the number of moles of each element in 100 g of caffeine.

$$moles\ C \quad = 49.18\ \cancel{g\,C}\ \frac{1\ mol\ C}{12.011\ \cancel{g\,C}} \quad = 4.095\ mol\ C$$

$$moles\ H \quad = 5.93\ \cancel{g\,H}\ \frac{1\ mol\ H}{1.0079\ \cancel{g\,H}} \quad = 5.35\ mol\ H$$

$$moles\ N \quad = 28.65\ \cancel{g\,N}\ \frac{1\ mol\ H}{14.0067\ \cancel{g\,H}} \quad = 2.045\ mol\ N$$

$$moles\ O \quad = 16.68\ \cancel{g\,O}\ \frac{1\ mol\ C}{15.9994\ \cancel{g\,O}} \quad = 1.043\ mol\ O$$

To obtain the relative numbers of atoms of each element present, divide the number of moles of each element by the number of moles of the element present in the least amount:

$$O: \frac{1.043}{1.043} = 1.000 \quad C: \frac{4.095}{1.043} = 3.926 \quad H: \frac{5.35}{1.043} = 5.13 \quad N: \frac{2.045}{1.043} = 1.960$$

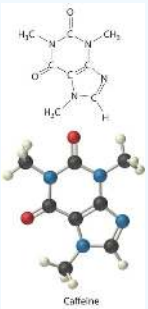
These results are fairly typical of actual experimental data. None of the atomic ratios is exactly integral but all are within 5% of integral values. Just as in Example 6, it is reasonable to assume that such small deviations from integral values are due to minor experimental errors, so round to the nearest integer. The empirical formula of caffeine is thus $C_4H_5N_2O$.

**B** The *molecular* formula of caffeine could be $C_4H_5N_2O$, but it could also be any integral multiple of this. To determine the actual molecular formula, we must divide the experimentally determined molar mass by the formula mass. The formula mass is calculated as follows:

Dividing the measured molar mass of caffeine (196 g/mol) by the calculated formula mass gives

$$\frac{196\ g/mol}{97.096\ g/C_4H_5N_2O} = 2.02 \approx 2C_4H_5N_2O$$

**C** There are two $C_4H_5N_2O$ formula units in caffeine, so the molecular formula must be $(C_4H_5N_2O)_2$ = $C_8H_{10}N_4O_2$. The structure of caffeine is as follows:




## Exercise 3.2.1

Calculate the molecular formula of Freon-114, which has 13.85% carbon, 41.89% chlorine, and 44.06% fluorine. The experimentally measured molar mass of this compound is 171 g/mol. Like Freon-11, Freon-114 is a commonly used refrigerant that has been implicated in the destruction of the ozone layer.

**Answer**

$C_2Cl_2F_4$

## Summary

The empirical formula of a substance can be calculated from the experimentally determined **percent composition**, the percentage of each element present in a pure substance by mass. In many cases, these percentages can be determined by *combustion analysis*. If the molar mass of the compound is known, the molecular formula can be determined from the empirical formula.

## Key Takeaway

- The empirical formula of a substance can be calculated from its percent composition, and the molecular formula can be determined from the empirical formula and the compound's molar mass.

## Conceptual Problems

1. What is the relationship between an empirical formula and a molecular formula?
2. Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 7.7 ) before proceeding to the Numerical Problems.*

1. What is the mass percentage of water in each hydrate?
    1. $H_3AsO_4 \cdot 0 \cdot 5H_2O$
    2. $NH_4NiCl_3 \cdot 6H_2O$
    3. $Al(NO_3)_3 \cdot 9H_2O$
2. What is the mass percentage of water in each hydrate?
    1. $CaSO_4 \cdot 2H_2O$
    2. $Fe(NO_3)_3 \cdot 9H_2O$
    3. $(NH_4)_3ZrOH(CO_3)_3 \cdot 2H_2O$
3. Which of the following has the greatest mass percentage of oxygen—$KMnO_4$, $K_2Cr_2O_7$, or $Fe_2O_3$?
4. Which of the following has the greatest mass percentage of oxygen—$ThOCl_2$, $MgCO_3$, or $NO_2Cl$?
5. Calculate the percent composition of the element shown in bold in each compound.
    1. Sb$\mathbf{Br}_3$
    2. $\mathbf{As}_2I_4$
    3. Al$\mathbf{P}O_4$
    4. $\mathbf{C}_6H_{10}O$
6. Calculate the percent composition of the element shown in bold in each compound.
    1. H$\mathbf{Br}O_3$
    2. $\mathbf{Cs}ReO_4$
    3. $\mathbf{C}_3H_8O$
    4. Fe$\mathbf{S}O_4$
7. A sample of a chromium compound has a molar mass of 151.99 g/mol. Elemental analysis of the compound shows that it contains 68.43% chromium and 31.57% oxygen. What is the identity of the compound?
8. The percentages of iron and oxygen in the three most common binary compounds of iron and oxygen are given in the following table. Write the empirical formulas of these three compounds.

| Compound | % Iron | % Oxygen | Empirical Formula |
|---|---|---|---|
| 1 | 69.9 | 30.1 | |
| 2 | 77.7 | 22.3 | |
| 3 | 72.4 | 27.6 | |

9. What is the mass percentage of water in each hydrate?
    1. $LiCl·H_2O$
    2. $MgSO_4·7H_2O$
    3. $Sr(NO_3)_2·4H_2O$
10. What is the mass percentage of water in each hydrate?
    1. $CaHPO_4·2H_2O$
    2. $FeCl_2·4H_2O$
    3. $Mg(NO_3)_2·4H_2O$
11. Two hydrates were weighed, heated to drive off the waters of hydration, and then cooled. The residues were then reweighed. Based on the following results, what are the formulas of the hydrates?

| Compound | Initial Mass (g) | Mass after Cooling (g) |
|---|---|---|
| $NiSO_4·xH_2O$ | 2.08 | 1.22 |
| $CoCl_2·xH_2O$ | 1.62 | 0.88 |

12. Which contains the greatest mass percentage of sulfur—$FeS_2$, $Na_2S_2O_4$, or $Na_2S$?
13. Given equal masses of each, which contains the greatest mass percentage of sulfur—$NaHSO_4$ or $K_2SO_4$?
14. Calculate the mass percentage of oxygen in each polyatomic ion.
    1. bicarbonate
    2. chromate
    3. acetate
    4. sulfite
15. Calculate the mass percentage of oxygen in each polyatomic ion.
    1. oxalate
    2. nitrite
    3. dihydrogen phosphate
    4. thiocyanate
16. The empirical formula of garnet, a gemstone, is $Fe_3Al_2Si_3O_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?
17. A compound has the empirical formula $C_2H_4O$, and its formula mass is 88 g. What is its molecular formula?
18. Mirex is an insecticide that contains 22.01% carbon and 77.99% chlorine. It has a molecular mass of 545.59 g. What is its empirical formula? What is its molecular formula?
19. How many moles of $CO_2$ and $H_2O$ will be produced by combustion analysis of 0.010 mol of styrene?



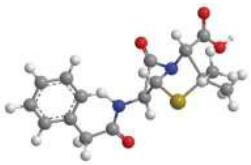
20. How many moles of $CO_2$, $H_2O$, and $N_2$ will be produced by combustion analysis of 0.0080 mol of aniline?




21. How many moles of $CO_2$, $H_2O$, and $N_2$ will be produced by combustion analysis of 0.0074 mol of aspartame?




22. How many moles of $CO_2$, $H_2O$, $N_2$, and $SO_2$ will be produced by combustion analysis of 0.0060 mol of penicillin G?




23. Combustion of a 34.8 mg sample of benzaldehyde, which contains only carbon, hydrogen, and oxygen, produced 101 mg of $CO_2$ and 17.7 mg of $H_2O$.
    1. What was the mass of carbon and hydrogen in the sample?
    2. Assuming that the original sample contained only carbon, hydrogen, and oxygen, what was the mass of oxygen in the sample?
    3. What was the mass percentage of oxygen in the sample?
    4. What is the empirical formula of benzaldehyde?
    5. The molar mass of benzaldehyde is 106.12 g/mol. What is its molecular formula?
24. Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of $CO_2$ and 17.0 mg of $H_2O$.
    1. What is the mass of oxygen in the sample?
    2. What is the mass percentage of oxygen in the sample?
    3. What is the empirical formula of salicylic acid?
    4. The molar mass of salicylic acid is 138.12 g/mol. What is its molecular formula?
25. Given equal masses of the following acids, which contains the greatest amount of hydrogen that can dissociate to form $H^+$—nitric acid, hydroiodic acid, hydrocyanic acid, or chloric acid?
26. Calculate the formula mass or the molecular mass of each compound.
    1. heptanoic acid (a seven-carbon carboxylic acid)
    2. 2-propanol (a three-carbon alcohol)
    3. $KMnO_4$
    4. tetraethyllead
    5. sulfurous acid
    6. ethylbenzene (an eight-carbon aromatic hydrocarbon)
27. Calculate the formula mass or the molecular mass of each compound.
    1. $MoCl_5$

2. $B_2O_3$
3. bromobenzene
4. cyclohexene
5. phosphoric acid
6. ethylamine

28. Given equal masses of butane, cyclobutane, and propene, which contains the greatest mass of carbon?

29. Given equal masses of urea [$(NH_2)_2CO$] and ammonium sulfate, which contains the most nitrogen for use as a fertilizer?

## Answers

1. To two decimal places, the percentages are:
    1. 5.97%
    2. 37.12%
    3. 43.22%
2. 
3. % oxygen: $KMnO_4$, 40.50%; $K_2Cr_2O_7$, 38.07%; $Fe_2O_3$, 30.06%
4. 
5. To two decimal places, the percentages are:
    1. 66.32% Br
    2. 22.79% As
    3. 25.40% P
    4. 73.43% C
6. 
7. $Cr_2O_3$.
8. 
9. To two decimal places, the percentages are:
    1. 29.82%
    2. 51.16%
    3. 25.40%
10. 
11. $NiSO_4 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$
12. 
13. $NaHSO_4$
14. 
15. 1. 72.71%
    2. 69.55%
    3. 65.99%
    4. 0%
16. 
17. $C_4H_8O_2$
18. 
19. 
20. 
21. 

22.

23. 1. 27.6 mg C and 1.98 mg H
    2. 5.2 mg O
    3. 15%
    4. $C_7H_6O$
    5. $C_7H_6O$

24.

25. hydrocyanic acid, HCN

26.

27. To two decimal places, the values are:

    1. 273.23 amu
    2. 69.62 amu
    3. 157.01 amu
    4. 82.14 amu
    5. 98.00 amu
    6. 45.08 amu

28.

29. Urea

## Contributors

- Anonymous

Modified by Joshua Halpern

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# 3.3: Chemical Equations

**Learning Objectives**

- To describe a chemical reaction.
- To calculate the quantities of compounds produced or consumed in a chemical reaction.bjective

As shown in Figure 3.3.1, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. We can describe this reaction with a chemical equationAn expression that gives the identities and quantities of the substances in a chemical reaction. Chemical formulas are used to indicate the reactants on the left and the products on the right. An arrow points from reactants to products., an expression that gives the identities and quantities of the substances in a chemical reaction. Chemical formulas and other symbols are used to indicate the starting material(s), or reactant(s)The starting material(s) in a chemical reaction., which by convention are written on the left side of the equation, and the final compound(s), or product(s)The final compound(s) produced in a chemical reaction., which are written on the right. An arrow points from the reactant to the products:

**Figure 3.3.1 An Ammonium Dichromate Volcano: Change during a Chemical Reaction**




The starting material (left) is solid ammonium dichromate. A chemical reaction (right) transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor. (In addition, energy in the form of heat and light is released.) During the reaction, the distribution of atoms changes, but the *number* of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced.

$$\underset{reactant}{(NH_4)_2\,Cr_2O_7} \quad \underset{products}{\rightarrow Cr_2O_3 + N^2 + 4H_2)} \tag{3.3.1}$$

The arrow is read as “yields” or “reacts to form.” So Equation 3.3.1 tells us that ammonium dichromate (the reactant) yields chromium(III) oxide, nitrogen, and water (the products).

The equation for this reaction is even more informative when written as

$$(NH_4)_2Cr_2O_7\,(s) \;\rightarrow\; Cr_2O_3\,(s) + N_2\,(g) + 4H_2O\,(g) \tag{3.3.2}$$

Equation 3.3.2 is identical to Equation 3.3.1 except for the addition of abbreviations in parentheses to indicate the physical state of each species. The abbreviations are (s) for solid, (l) for liquid, (g) for gas, and (aq) for an *aqueous solution*, a solution of the substance in water.

Consistent with the law of conservation of mass, the numbers of each type of atom are the same on both sides of Equation 3.3.1 and Equation 3.3.2. (For more information on the law of conservation of mass, see Section 1.4) As illustrated in Figure 3.3.1, each side has two chromium atoms, seven oxygen atoms, two nitrogen atoms, and eight hydrogen atoms. In a *balanced chemical equation*, both the numbers of each type of atom and the total charge are the same on both sides. Equation 3.3.1 and Equation 3.3.2 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. *A chemical reaction represents a change in the distribution of atoms but not in the number of atoms*. In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, *the equation must first be balanced*.

### Note the Pattern

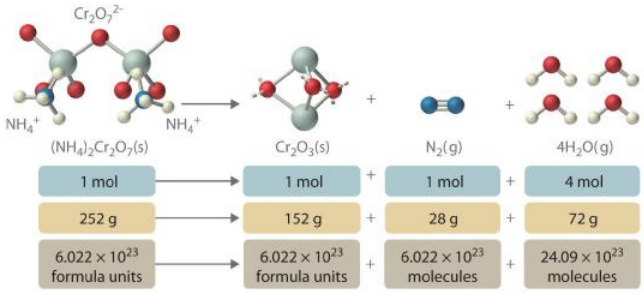
A chemical reaction changes only the distribution of atoms, *not* the number of atoms.

## Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides *quantitative* information. Specifically, it tells the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficientA number greater than 1 preceding a formula in a balanced chemical equation and indicating the number of atoms, molecules, or formula units of a reactant or a product. of that species (e.g., the 4 preceding $H_2O$ in Equation 7.3.2). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 3.3.2, the coefficients allow us to interpret Equation 7.3.1 in any of the following ways:

- Two $NH_4^+$ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of $Cr_2O_3$, 1 $N_2$ molecule, and 4 $H_2O$ molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of $Cr_2O_3$, 1 mol of $N_2$, and 4 mol of $H_2O$.
- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of $Cr_2O_3$, 28 g of $N_2$, and 72 g of $H_2O$.
- A total of $6.022 \times 10^{23}$ formula units of $(NH_4)_2Cr_2O_7$ yields $6.022 \times 10^{23}$ formula units of $Cr_2O_3$, $6.022 \times 10^{23}$ molecules of $N_2$, and $24.09 \times 10^{23}$ molecules of $H_2O$.

**Figure 3.3.2 The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano**




These are all *chemically equivalent* ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratioThe ratio of the number of moles of one substance to the number of moles of another, as depicted by a balanced chemical equation.. For example, the mole ratio of $H_2O$ to $N_2$ in Equation 3.3.1 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass: 252 g of $(NH_4)_2Cr_2O_7$ yields 152 + 28 + 72 = 252 g of products. The chemical equation does *not*, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. We will consider these issues in more detail in the second semester.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy,

carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call *combustion*. Based on these experiments, he proposed that "Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal." Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

### Example 3.3.1

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \;\rightarrow\; 6CO_2\,(g) + 6H_2O\,(l)$$

Construct a table showing how to interpret the information in this equation in terms of

1. a single molecule of glucose.
2. moles of reactants and products.
3. grams of reactants and products represented by 1 mol of glucose.
4. numbers of molecules of reactants and products represented by 1 mol of glucose.

**Given:** balanced chemical equation

**Asked for:** molecule, mole, and mass relationships

**Strategy:**

**A** Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.

**B** Use the molar masses of the reactants and products to convert from moles to grams.

**C** Use Avogadro's number to convert from moles to the number of molecules.

**Solution**

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

**A** One molecule of glucose reacts with 6 molecules of $O_2$ to yield 6 molecules of $CO_2$ and 6 molecules of $H_2O$.

**B** One mole of glucose reacts with 6 mol of $O_2$ to yield 6 mol of $CO_2$ and 6 mol of $H_2O$.

**C** To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; $O_2$, 31.9988; $CO_2$, 44.010; and $H_2O$, 18.015.

$$\begin{array}{ccc} mass\ of\ reactants & = & mass\ of\ products \\ g\ glucose & = & g\ CO_2 + g\ H_2O \end{array}$$

$$1\ \cancel{mol\ glucose}\left(\frac{180.16\ g}{1\ \cancel{mol\ glucose}}\right) + 6\ \cancel{mol\ O_2}\left(\frac{31.9988\ g}{1\ \cancel{mol\ O_2}}\right)\cancel{\left(\frac{6\ mol\ CO_2}{\ }\right)}\left(\frac{44.010\ g}{1\ \cancel{mol\ CO_2}}\right) + 6\ \cancel{mol\ H_2O}\left(\frac{18.0158\ g}{1\ \cancel{mol\ H_2O}}\right)$$

$$372.15\ g \;=\; 372.15\ g$$

1. **C** One mole of glucose contains Avogadro's number ($6.022 \times 10^{23}$) of glucose molecules. Thus $6.022 \times 10^{23}$ glucose molecules react with ($6 \times 6.022 \times 10^{23}$) = $3.613 \times 10^{24}$ oxygen molecules to yield ($6 \times 6.022 \times 10^{23}$) = $3.613 \times 10^{24}$ molecules each of $CO_2$ and $H_2O$.

   In tabular form:

| | $C_6H_{12}O_6(s)$ | + | $6O_2(g)$ | → | $6CO_2(g)$ | + | $6H_2O(l)$ |
|---|---|---|---|---|---|---|---|
| a. | 1 molecule | | 6 molecules | | 6 molecules | | 6 molecules |
| b. | 1 mol | | 6 mol | | 6 mol | | 6 mol |
| c. | 180.16 g | | 191.9928 g | | 264.06 g | | 108.09 g |
| d. | $6.022 \times 10^{23}$ molecules | | $3.613 \times 10^{24}$ molecules | | $3.613 \times 10^{24}$ molecules | | $3.613 \times 10^{24}$ molecules |

## Exercise 3.3.1

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas. The explosion resulted from the following reaction:

$$2NH_4NO_3\,(s) \rightarrow 2N_2\,(g) + 4H_2O\,(g) + O_2\,(g)$$

Construct a table showing how to interpret the information in the equation in terms of

1. individual molecules and ions.
2. moles of reactants and products.
3. grams of reactants and products given 2 mol of ammonium nitrate.
4. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

**Answer**

| | $2NH_4NO_3(s)$ | → | $2N_2(g)$ | + | $4H_2O(g)$ | + | $O_2(g)$ |
|---|---|---|---|---|---|---|---|
| a. | $2NH_4^+$ ions and $2NO_3^-$ ions | | 2 molecules | | 4 molecules | | 1 molecule |
| b. | 2 mol | | 2 mol | | 4 mol | | 1 mol |
| c. | 160.0864 g | | 56.0268 g | | 72.0608 g | | 31.9988 g |
| d. | $1.204 \times 10^{24}$ formula units | | $1.204 \times 10^{24}$ molecules | | $2.409 \times 10^{24}$ molecules | | $6.022 \times 10^{23}$ molecules |



**Ammonium nitrate can be hazardous.** This aerial photograph of Texas City, Texas, shows the devastation caused by the explosion of a shipload of ammonium nitrate on April 16, 1947.

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas. The explosion resulted from the following reaction:

$$2NH_4NO_3\,(s) \;\rightarrow\; 2N_2\,(g) + 4H_2O\,(g) + O_2\,(g)$$

Construct a table showing how to interpret the information in the equation in terms of

1. individual molecules and ions.
2. moles of reactants and products.
3. grams of reactants and products given 2 mol of ammonium nitrate.
4. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

**Answer**

## Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of *n*-heptane ($C_7H_{16}$), an important component of gasoline:

$$C_7H_{16}\,(l) + O_2\,(g) \;\rightarrow\; CO_2\,(g) + H_2O\,(g) \tag{3.3.3}$$

The complete combustion of any hydrocarbon with sufficient oxygen *always* yields carbon dioxide and water ( Figure 3.3.3 ).

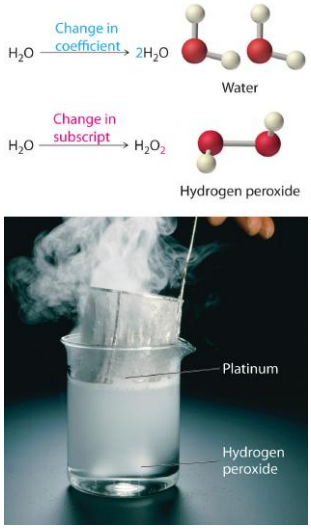
**Figure 3.3.3 An Example of a Combustion Reaction**




*The wax in a candle is a high-molecular-mass hydrocarbon, which produces gaseous carbon dioxide and water vapor in a combustion reaction. When the candle is allowed to burn inside a flask, drops of water, one of the products of combustion, form which we can verify using cobalt chloride test paper. We can demonstrate that carbon dioxide is a product by precipitating calcium carbonate from limewater..*

Equation 3.3.3 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, we must adjust the coefficients of the reactants and products to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, we *cannot* balance the equation by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 3.3.4.

**Figure 3.3.4 Balancing Equations**




You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water ($H_2O$) and hydrogen peroxide ($H_2O_2$) are chemically distinct substances. $H_2O_2$ decomposes to $H_2O$ and $O_2$ gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. We present an efficient approach to balancing a chemical equation using this method.

## Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

To demonstrate this approach, let’s use the combustion of *n*-heptane (Equation 3.3.3) as an example.

1. **Identify the most complex substance.** The most complex substance is the one with the largest number of different atoms, which is $C_7H_{16}$. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.** Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of *n*-heptane contains 7 carbon atoms, we need 7 $CO_2$ molecules, each of which contains 1 carbon atom, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7CO_2 + H_2O \tag{3.3.4}$$

3. **Balance polyatomic ions as a unit.** There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.** Because one molecule of *n*-heptane contains 16 hydrogen atoms, we need 8 $H_2O$ molecules, each of which contains 2 hydrogen atoms, on the right side:

$$C_7H_{16} + O_2 \rightarrow \ 7CO_2 + 8H_2O \tag{3.3.5}$$

5. The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, $O_2$, on the reactant side:

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \tag{3.3.6}$$

6. **Check your work.** The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. *Always check to be sure that a chemical equation is balanced.*

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. Consider, for example, a similar reaction, the combustion of isooctane ($C_8H_{18}$). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

$$C_8H_{18}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g) \tag{3.3.7}$$

1. **Identify the most complex substance.** Begin the balancing process by assuming that the final balanced chemical equation contains a single molecule of isooctane.
2. **Adjust the coefficients.** The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 $CO_2$ molecules in the products:

$$C_8H_{18}\,(l) + O_2\,(g) \rightarrow 8CO_2\,(g) + H_2O\,(g) \tag{3.3.8}$$

3. **Balance polyatomic ions as a unit.** This step does not apply to this equation.
4. **Balance the remaining atoms.** Eighteen hydrogen atoms in isooctane means that there must be 9 $H_2O$ molecules in the products:

$$C_8H_{18}\,(l) + O_2\,(g) \rightarrow 8CO_2\,(g) + 9H_2O\,(g) \tag{3.3.9}$$

The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, $O_2$, but because there are 2 oxygen atoms per $O_2$ molecule, we must use a fractional coefficient (25/2) to balance the oxygen atoms:

$$C_8H_{18}\,(l) + 25/2O_2\,(g) \rightarrow 8CO_2\,(g) + 9H_2O\,(g) \tag{3.3.10}$$

Equation 7.3.10 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$2C_8H_{18}\,(l) + 25O_2\,(g) \rightarrow 16CO_2\,(g) + 18H_2O\,(g) \tag{3.3.11}$$

5. **Check your work.** The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.

Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

**Example 3.3.1**

The reaction of the mineral hydroxyapatite [$Ca_5(PO_4)_3(OH)$] with phosphoric acid and water gives $Ca(H_2PO_4)_2{\cdot}H_2O$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.

**Given:** reactants and product

**Asked for:** balanced chemical equation

**Strategy:**

**A** Identify the product and the reactants and then write the unbalanced chemical equation.

**B** Follow the steps for balancing a chemical equation.

**Solution**

We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem. Recall that phosphoric acid is $H_3PO_4$. The initial (unbalanced) equation is as follows:

$$Ca_5(PO_4)_3(OH)(s) + H_3PO_4(aq) + H_2O(l) \rightarrow Ca(H_2PO_4)_2 \cdot H_2O(s)$$

1. **Identify the most complex substance.** We start by assuming that only one molecule or formula unit of the most complex substance, $Ca_5(PO_4)_3(OH)$, appears in the balanced chemical equation.
2. **Adjust the coefficients.** Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $Ca_5(PO_4)_3(OH)$ contains 5 calcium atoms, so we need 5 $Ca(H_2PO_4)_2 \cdot H_2O$ on the right side:

$$Ca_5(PO_4)_3(OH) + H_3PO_4 + H_2O \rightarrow 5Ca(H_2PO_4)_2 \cdot H_2O$$

3. **Balance polyatomic ions as a unit.** It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion ($PO_4^{3-}$), shows up in three places.In $H_3PO_4$, the phosphate ion is combined with three $H^+$ ions to make phosphoric acid ($H_3PO_4$), whereas in $Ca(H_2PO_4)_2 \cdot H_2O$ it is combined with two $H^+$ ions to give the dihydrogen phosphate ion. Thus it is easier to balance $PO_4$ as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 $PO_4$ units on the right side but only 4 on the left. The simplest way to balance the $PO_4$ units is to place a coefficient of 7 in front of $H_3PO_4$:

$$Ca_5(PO_4)_3(OH) + 7H_3PO_4 + H_2O \rightarrow 5Ca(H_2PO_4)_2 \cdot H_2O$$

   Although $OH^-$ is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

4. **Balance the remaining atoms.** We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, $H_2O$, by placing a coefficient of 4 in front of $H_2O$ on the left side, giving a total of 4 $H_2O$ molecules:

$$Ca_5(PO_4)_3(OH)(s) + 7H_3PO_4(aq) + 4H_2O(l) \rightarrow 5Ca(H_2PO_4)_2 \cdot H_2O(s)$$

   The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 45 oxygen atoms on each side.

5. **Check your work.** Both sides of the equation contain 5 calcium atoms, 7 phosphorus atoms, 30 hydrogen atoms, and 45 oxygen atoms.

## ? Exercise 3.3.1

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol and carbon dioxide. Write a balanced chemical reaction for the fermentation of glucose.



**Commercial use of fermentation.** (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.

**Answer**

$$C_6H_{12}O_6\,(s)\ \rightarrow\ 2C_2H_5OH\,(l) + 2CO_2\,(g)$$

## Summary

In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a *balanced chemical equation*, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

## Key Takeaway

- A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products.

## Conceptual Problems

1. How does a balanced chemical equation agree with the law of definite proportions?
2. What is the difference between $S_8$ and 8S? Use this example to explain why subscripts in a formula must not be changed.
3. What factors determine whether a chemical equation is balanced?
4. What information can be obtained from a balanced chemical equation? Does a balanced chemical equation give information about the rate of a reaction?

## Numerical Problems

1. Balance each chemical equation.
    1. $KI(aq) + Br_2(l) \rightarrow KBr(aq) + I_2(s)$
    2. $MnO_2(s) + HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + H_2O(l)$
    3. $Na_2O(s) + H_2O(l) \rightarrow NaOH(aq)$
    4. $Cu(s) + AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + Ag(s)$
    5. $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
    6. $S_2Cl_2(l) + NH_3(l) \rightarrow S_4N_4(s) + S_8(s) + NH_4Cl(s)$
2. Balance each chemical equation.
    1. $Be(s) + O_2(g) \rightarrow BeO(s)$
    2. $N_2O_3(g) + H_2O(l) \rightarrow HNO_2(aq)$

3. $Na(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$
4. $CaO(s) + HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l)$
5. $CH_3NH_2(g) + O_2(g) \rightarrow H_2O(g) + CO_2(g) + N_2(g)$
6. $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$

3. Balance each chemical equation.

1. $N_2O_5(g) \rightarrow NO_2(g) + O_2(g)$
2. $NaNO_3(s) \rightarrow NaNO_2(s) + O_2(g)$
3. $Al(s) + NH_4NO_3(s) \rightarrow N_2(g) + H_2O(l) + Al_2O_3(s)$
4. $C_3H_5N_3O_9(l) \rightarrow CO_2(g) + N_2(g) + H_2O(g) + O_2(g)$
5. reaction of butane with excess oxygen
6. $IO_2F(s) + BrF_3(l) \rightarrow IF_5(l) + Br_2(l) + O_2(g)$

4. Balance each chemical equation.

1. $H_2S(g) + O_2(g) \rightarrow H_2O(l) + S_8(s)$
2. $KCl(aq) + HNO_3(aq) + O_2(g) \rightarrow KNO_3(aq) + Cl_2(g) + H_2O(l)$
3. $NH_3(g) + O_2(g) \rightarrow NO(g) + H_2O(g)$
4. $CH_4(g) + O_2(g) \rightarrow CO(g) + H_2(g)$
5. $NaF(aq) + Th(NO_3)_4(aq) \rightarrow NaNO_3(aq) + ThF_4(s)$
6. $Ca_5(PO_4)_3F(s) + H_2SO_4(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + CaSO_4 \cdot 2H_2O(s) + HF(aq)$

5. Balance each chemical equation.

1. $NaCl(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$
2. $K(s) + H_2O(l) \rightarrow KOH(aq) + H_2(g)$
3. reaction of octane with excess oxygen
4. $S_8(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$
5. $CH_3OH(l) + I_2(s) + P_4(s) \rightarrow CH_3I(l) + H_3PO_4(aq) + H_2O(l)$
6. $(CH_3)_3Al(s) + H_2O(l) \rightarrow CH_4(g) + Al(OH)_3(s)$

6. Write a balanced chemical equation for each reaction.

1. Aluminum reacts with bromine.
2. Sodium reacts with chlorine.
3. Aluminum hydroxide and acetic acid react to produce aluminum acetate and water.
4. Ammonia and oxygen react to produce nitrogen monoxide and water.
5. Nitrogen and hydrogen react at elevated temperature and pressure to produce ammonia.
6. An aqueous solution of barium chloride reacts with a solution of sodium sulfate.

7. Write a balanced chemical equation for each reaction.

1. Magnesium burns in oxygen.
2. Carbon dioxide and sodium oxide react to produce sodium carbonate.
3. Aluminum reacts with hydrochloric acid.
4. An aqueous solution of silver nitrate reacts with a solution of potassium chloride.
5. Methane burns in oxygen.
6. Sodium nitrate and sulfuric acid react to produce sodium sulfate and nitric acid.

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# 3.4: Mass Relationships in Chemical Equations

**Learning Objectives**

- To calculate the quantities of compounds produced or consumed in a chemical reaction.

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced. Stoichiometry is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. A stoichiometric quantity is the amount of product or reactant specified by the coefficients in a balanced chemical equation. In Section 7.3 , for example, you learned how to express the stoichiometry of the reaction for the ammonium dichromate volcano in terms of the atoms, ions, or molecules involved and the numbers of moles, grams, and formula units of each (recognizing, for instance, that 1 mol of ammonium dichromate produces 4 mol of water). This section describes how to use the stoichiometry of a reaction to answer questions like the following: How much oxygen is needed to ensure complete combustion of a given amount of isooctane? (This information is crucial to the design of nonpolluting and efficient automobile engines.) How many grams of pure gold can be obtained from a ton of low-grade gold ore? (The answer determines whether the ore deposit is worth mining.) If an industrial plant must produce a certain number of tons of sulfuric acid per week, how much elemental sulfur must arrive by rail each week?

All these questions can be answered using the concepts of the mole and molar and formula masses, along with the coefficients in the appropriate balanced chemical equation.

## Stoichiometry Problems

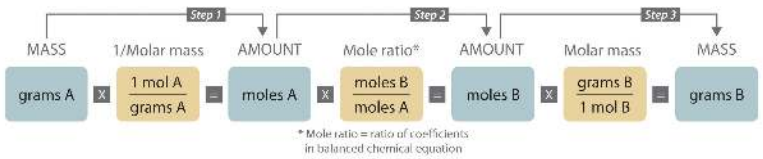
When we carry out a reaction in either an industrial setting or a laboratory, it is easier to work with *masses* of substances than with the numbers of molecules or moles. The general method for converting from the mass of any reactant or product to the mass of any other reactant or product using a balanced chemical equation is outlined in Figure 3.4.1 and described in the following text.

## Steps in Converting between Masses of Reactant and Product

1. Convert the mass of one substance (substance A) to the corresponding number of moles using its molar mass.
2. From the balanced chemical equation, obtain the number of moles of another substance (B) from the number of moles of substance A using the appropriate mole ratio (the ratio of their coefficients).
3. Convert the number of moles of substance B to mass using its molar mass. It is important to remember that some species are in excess by virtue of the reaction conditions. For example, if a substance reacts with the oxygen in air, then oxygen is in obvious (but unstated) excess.

Converting amounts of substances to moles—and vice versa—is the key to all stoichiometry problems, whether the amounts are given in units of mass (grams or kilograms), weight (pounds or tons), or volume (liters or gallons).

**Figure 3.4.1 A Flowchart for Stoichiometric Calculations Involving Pure Substances**




The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.

To illustrate this procedure, let's return to the combustion of glucose. We saw earlier that glucose reacts with oxygen to produce carbon dioxide and water:

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \rightarrow 6CO_2\,(g) + 6H_2O\,(l) \tag{3.4.1}$$

Just before a chemistry exam, suppose a friend reminds you that glucose is the major fuel used by the human brain. You therefore decide to eat a candy bar to make sure that your brain doesn't run out of energy during the exam (even though there is no direct evidence that consumption of candy bars improves performance on chemistry exams). If a typical 2 oz candy bar contains the equivalent of 45.3 g of glucose and the glucose is completely converted to carbon dioxide during the exam, how many grams of carbon dioxide will you produce and exhale into the exam room?

The initial step in solving a problem of this type must be to write the balanced chemical equation for the reaction. Inspection of Eq 3.4.1 shows that it is balanced as written, so we can proceed to the strategy outlined in Figure 3.4.1, adapting it as follows:

1. Use the molar mass of glucose (to one decimal place, 180.2 g/mol) to determine the number of moles of glucose in the candy bar: $moles\ glucose = 45.3\ \cancel{g\ glucose} \times \dfrac{1\ mol\ glucose}{180.2\ \cancel{g\ glucose}} = 0.251\ mol\ glucose$
2. According to the balanced chemical equation, 6 mol of $CO_2$ is produced per mole of glucose; the mole ratio of $CO_2$ to glucose is therefore 6:1. If we divide the number of moles of CO2 by its stoichiometric coefficient 6 and the number of moles of glucose by its stoichiometric coefficient of one the ratios, which can be called the reaction equivalents, are equal. (Step 2a) We will use this below in demonstrating another method of solving stoichiometric problems of all types

$$\frac{moles\ CO_2}{6\ mol\ CO_2} = \frac{moles\ glucose}{1\ mol\ glucose}$$

The number of moles of $CO_2$ produced is thus

$$\begin{aligned} molesCO_2 &= mol\ glucose \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \\ &= 0.251\ \cancel{mol\ glucose} \times \frac{6\ mol\ CO_2}{1\ \cancel{mol\ glucose}} \\ &= 1.51\ mol\ CO_2 \end{aligned}$$

3. Use the molar mass of $CO_2$ (44.010 g/mol) to calculate the mass of $CO_2$ corresponding to 1.51 mol of $CO_2$:

\( mass\; of\; CO_{2}=1.51\; \cancel{mol\; CO_{2}}\times \dfrac{44.010\; g\; CO_{2}}{1\; \cancel{mol\; CO_{2}}}=66.5\; g\; CO_{2} \notag \)

4 We can summarize these operations as follows:

$$45.3\ g\ glucose \underset{step\ 1}{\times \frac{1\ mol\ glucose}{180.2\ g\ glucose}} \underset{step\ 2}{\times \frac{6\ mol\ CO_2}{1\ mol\ glucose}} \underset{step\ 3}{\times \frac{44.010\ g\ CO_2}{1\ mol\ CO_2}} = 66.4\ g\ CO_2$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. (For more information about rounding and significant digits. (See Essential Skills 1 in Section 1.10) In Chapter 9, you will discover that this amount of gaseous carbon dioxide occupies an enormous volume—more than 33 L. We could use similar methods to calculate the amount of oxygen consumed or the amount of water produced.

We just used the balanced chemical equation to calculate the mass of product that is formed from a certain amount of reactant. We can also use the balanced chemical equation to determine the masses of reactants that are necessary to form a certain amount of product or, as shown in Example 11, the mass of one reactant that is required to consume a given mass of another reactant.

There is another way of dealing with such problems which is easier to carry out. It starts by writing the balanced chemical equation and then drawing a table with five rows and as many columns as there are reactants and products and writing in the Mass of the given reactant

| | $C_6H_{12}O_6(s)$ | $+ 6O_2(g)$ | $\rightarrow 6CO_2(g)$ | $+ 6H_2O(l)$ |
|---|---|---|---|---|
| Mass (g) | 45.3 | | | |
| Molecular Weight (g/mol) | | | | |
| Moles | | | | |
| Stoichiometric Coefficients | | | | |
| Stoichiometric Equivalents | | | | |

We then simply fill in the stoichiometric coefficients and the molecular weights of the reactants and the products that we are concerned with

| | $C_6H_{12}O_6(s)$ | $+ 6O_2(g)$ | $\rightarrow 6CO_2(g)$ | $+ 6H_2O(l)$ |
|---|---|---|---|---|
| Mass (g) | 45.3 | | | |
| Molecular Weight (g/mol) | 180.2 | | | |
| Moles | | | | |
| Stoichiometric Coefficients | 1 | | 6 | |
| Stoichiometric Equivalents | | | | |

Then divide the mass of the glucose by the molecular weight to find the number of moles of glucose. In the next step divide the number of moles by the stoichiometric coefficient to find the stoichiometric equivalents (this is the same as step 2a above. The rule is to divide going down the table. You divide the Mass by the Molecular Weight to find the number of Moles, you divide the number of Moles by the Stoichiometric Coefficients to find the number of Stoichiometric Equivalents

| | $C_6H_{12}O_6(s)$ | $+ 6O_2(g)$ | $\rightarrow 6CO_2(g)$ | $+ 6H_2O(l)$ |
|---|---|---|---|---|
| Mass (g) | 45.3 | | | |
| Molecular Weight (g/mol) | 180.2 | | | |
| Moles | 0.251 | | | |
| Stoichiometric Coefficients | 1 | | 6 | |
| Stoichiometric Equivalents | 0.251 | | | |

For each of the products and reactants, the Stoichiometric Equivalents will be the same (they are equivalent, simply copy across).

| | $C_6H_{12}O_6(s)$ | $+ 6O_2(g)$ | $\rightarrow 6CO_2(g)$ | $+ 6H_2O(l)$ |
|---|---|---|---|---|
| Mass (g) | 45.3 | | 66.4 | |
| Molecular Weight (g/mol) | 180.2 | | 44.01 | |
| Moles | 0.251 | | 1.51 | |
| Stoichiometric Coefficients | 1 | | 6 | |
| Stoichiometric Equivalents | 0.251 | | 0.251 | |

Now multiply going up. Multiply the Stoichiometric Equivalents by the Stoichiometric Coefficient to find the number of Moles of $CO_2$ then multiply the number of Moles of CO2 by the Molecular Weight of CO2 to find the Mass of CO2 produced in the reaction. Close inspection of both methods will show that they are equivalent. The table has the advantage that it is a "fill in the spaces" exercise, and practically automatic. In fact you could easily write an Excel spreadsheet to do it. The table method has advantages if we want to answer question such as how much water will be produced or how much oxygen will be consumed. It also is simpler for more complicated limiting reagent problems.

As an example, we can now figure out how much oxygen is used up and how much water will be produced by this reaction. Simply use the same method as for the CO2.

| | $C_6H_{12}O_6(s)$ | $+ 6O_2(g)$ | $\rightarrow 6CO_2(g)$ | $+ 6H_2O(l)$ |
|---|---|---|---|---|
| Mass (g) | 45.3 | 48.32 | 66.4 | 27.2 |
| Molecular Weight (g/mol) | 180.2 | 32.00 | 44.01 | 18.02 |
| Moles | 0.251 | 1.51 | 1.51 | 1.51 |
| Stoichiometric Coefficients | 1 | 6 | 6 | 6 |
| Stoichiometric Equivalents | 0.251 | 0.251 | 0.251 | 0.251 |

Notice that all of the Stoichiometric Equivalents are the same and that we multiply the Stoichiometric Equivalents by the Stoichiometric Coefficients to find the number of Moles, and the number of Moles by the Molecular Weight to find the Mass.

**Example 3.4.1**

The combustion of hydrogen with oxygen to produce gaseous water is extremely vigorous, producing one of the hottest flames known. Because so much energy is released for a given mass of hydrogen or oxygen, this reaction was used to fuel the NASA (National Aeronautics and Space Administration) space shuttles, which have recently been retired from service. NASA engineers calculated the exact amount of each reactant needed for the flight to make sure that the shuttles did not carry excess fuel into orbit. Calculate how many tons of hydrogen a space shuttle needed to carry for each 1.00 tn of oxygen (1 tn = 2000 lb).



**The US space shuttle *Discovery* during liftoff.** The large cylinder in the middle contains the oxygen and hydrogen that fueled the shuttle's main engine.

**Given:** reactants, products, and mass of one reactant

**Asked for:** mass of other reactant

**Strategy:**

**A** Write the balanced chemical equation for the reaction.

**B** Convert mass of oxygen to moles. From the mole ratio in the balanced chemical equation, determine the number of moles of hydrogen required. Then convert the moles of hydrogen to the equivalent mass in tons.

**Solution**

We use the same general strategy for solving stoichiometric calculations as in the preceding example. Because the amount of oxygen is given in tons rather than grams, however, we also need to convert tons to units of mass in grams. Another conversion is needed at the end to report the final answer in tons.

**A** We first use the information given to write a balanced chemical equation. Because we know the identity of both the reactants and the product, we can write the reaction as follows:

$$H_2\,(g) + O_2\,(g) \;\rightarrow H_2O\,(g)$$

This equation is not balanced because there are two oxygen atoms on the left side and only one on the right. Assigning a coefficient of 2 to both $H_2O$ and $H_2$ gives the balanced chemical equation:

$$2H_2\,(g) + O_2\,(g) \;\rightarrow 2H_2O\,(g)$$

Thus 2 mol of $H_2$ react with 1 mol of $O_2$ to produce 2 mol of $H_2O$.

**B** To convert tons of oxygen to units of mass in grams, we multiply by the appropriate conversion factors:

$$mass\ of\ O_2 = 1.0\ \cancel{tn} \times \frac{2000\ \cancel{lb}}{\cancel{tn}} \times \frac{4453.6\ g}{\cancel{lb}} = 9.07 \times 10^5\ g\ O_2$$

Using the molar mass of $O_2$ (32.00 g/mol to four significant figures) we can calculate the number of moles of $O_2$ contained in this mass of $O_2$

$$mol\ O_2 = 9.07 \times 10^5\ \cancel{g\ O_2} \times \frac{1\ mol\ O_2}{32.00\ \cancel{g\ O_2}} = 2.83 \times 10^4\ mol\ O_2$$

1. Now use the coefficients in the balanced chemical equation to obtain the number of moles of $H_2$ needed to react with this number of moles of $O_2$:
2. The molar mass of $H_2$ (2.016 g/mol) allows us to calculate the corresponding mass of $H_2$:

   Finally, convert the mass of $H_2$ to the desired units (tons) by using the appropriate conversion factors:

The space shuttle had to be designed to carry 0.126 tn of $H_2$ for each 1.00 tn of $O_2$. Even though 2 mol of $H_2$ are needed to react with each mole of $O_2$, the molar mass of $H_2$ is so much smaller than that of $O_2$ that only a relatively small mass of $H_2$ is needed compared to the mass of $O_2$.

**? Exercise 3.4.1**

Alchemists produced elemental mercury by roasting the mercury-containing ore cinnabar (HgS) in air:

$$HgS\,(s) + O_2\,(g) \;\rightarrow\; Hg\,(l) + SO_2\,(g)$$

The volatility and toxicity of mercury make this a hazardous procedure, which likely shortened the life span of many alchemists. Given 100 g of cinnabar, how much elemental mercury can be produced from this reaction?

**Answer**

86.2 g

## Limiting Reactants

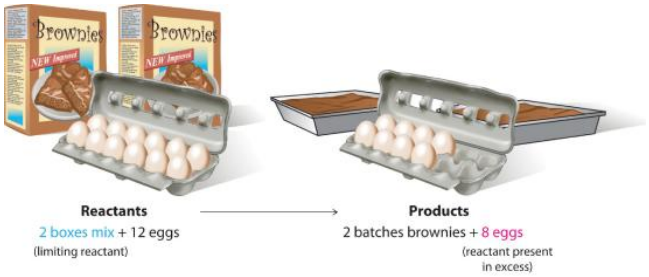
In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is *in excess*.

To be certain you understand these concepts, let's first consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1\ box\ mix + 2\ eggs \;\rightarrow\; 1\ batch\ brownies \tag{3.4.2}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in Eq 3.4.2 is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant (Figure 3.4.2 ). Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

Figure 3.4.2 The Concept of a Limiting Reactant in the Preparation of Brownies




Let's now turn to a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth's crust, it is relatively difficult to extract from its ores.

In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($TiCl_4$) and carbon dioxide. Titanium tetrachloride is then converted to metallic titanium by reaction with magnesium metal at high temperature:

$$TiCl_4\,(g) + 2Mg\,(l) \;\rightarrow\; Ti\,(s) + 2MgCl_2\,(l) \tag{3.4.3}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances economically one would want to maximize the use of magnesium making sure that none was left during the production of titanium metal. If a little bit of the titanium (IV) chloride were left over that would not be so concerning.



**Medical use of titanium.** Here is an example of its successful use in joint replacement implants.

Suppose you have 1.00 kg of titanium tetrachloride and 200 g of magnesium metal. How much titanium metal can you produce according to Equation 3.4.3 ? Solving this type of problem requires that you carry out the following steps:

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

1. To determine the number of moles of reactants present, you must calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$moles TiCl_4 = \frac{mass\ TiCl_4}{molar\ mass\ TiCl_4}$$

$$= 1000\ \cancel{g\ TiCl_4} \times \frac{1\ mol\ TiCl_4}{189.679\ \cancel{g\ TiCl_4}} = 5.272\ mol\ TiCl_4$$

$$moles Mg = \frac{mass\ Mg}{molar\ mass\ Mg}$$

$$= 200\ \cancel{g\ Mg} \times \frac{1\ mol\ Mg}{24.305\ \cancel{g\ Mg}} = 8.23\ mol\ Mg$$

2. You have more moles of magnesium than of titanium tetrachloride, but the ratio is only

$$\frac{mol\ Mg}{mol\ TiCl_4} = \frac{8.23\ mol}{5.272\ mol} = 1.56$$

Because the ratio of the coefficients in the balanced chemical equation is

$$\frac{2\ mol\ Mg}{1 mol\ TiCl_4} = 2$$

you do not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, you should calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, you have 8.23 mol of Mg, so you need (8.23 ÷ 2) = 4.12 mol of $TiCl_4$ for complete reaction. Because you have 5.272 mol of $TiCl_4$, titanium tetrachloride *is present in excess*. Conversely, 5.272 mol of $TiCl_4$ requires 2 × 5.272 = 10.54 mol of Mg, but you have only 8.23 mol. So *magnesium is the limiting reactant.*

3. Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed: $moles\ Ti = 8.23\ \cancel{mol\ Mg} \times \dfrac{1\ molTi}{2\ \cancel{mol\ Mg}} = 4.12\ mol\ Ti$

   Thus only 4.12 mol of Ti can be formed.

4. To calculate the mass of titanium metal that you can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$moles\ Ti = mass\ Ti \times molar\ mass\ Ti = 4.12\ \cancel{mol\ Ti} \times \frac{47.867\ g\ Ti}{1\ mol\ Ti} = 197\ g\ Ti$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of $TiCl_4$ and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

$$TiCl_4: \frac{5.272\ mol\ (actual)}{1\ mol\ \ (stoich)} = 5.272 \quad Mg: \frac{8.23\ mol\ (actual)}{2\ mol\ \ (stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Below the same problem is written out starting with the balanced reaction, the Mass of the reactants and the Molecular Mass of both. First divide the Mass by the Molecular Weight to find the number of Moles of each reactant. After that divide the number of Moles by the Stoichiometric Coefficients to find the Stoichiometric Equivalents.

| | $TiCl_4$(s) | + 2Mg(s) | → $2MgCl_2$(s) | + Ti(s) |
|---|---|---|---|---|
| Mass (g) | 1000 | 200 | | |
| Molecular Weight (g/mol) | 189.67 | 24.31 | | |
| Moles | 5.27 | 8.23 | | |
| Stoichiometric Coefficients | 1 | 2 | | |
| Stoichiometric Equivalents | 5.27 | 4.11 | | |

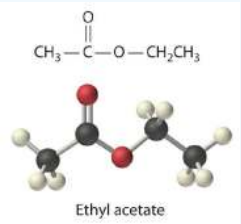
Because the number of Stoichiometric Equivalents for the Mg is smaller, it is the limiting reagant. We now simply carry out the Table calculation for Ti(s) to find the mass of Ti produced. Similarly we could calculate the mass of $MgCl_2$(s) produced or even the amount of $TiCl_4$(s) that was consumed in the reaction. Remember we divide going down the table and multiply going up.

| | $TiCl_4$(s) | + 2Mg(s) | → $2MgCl_2$(s) | + Ti(s) |
|---|---|---|---|---|
| Mass (g) | 1000 | 200 | | 196.9 |
| Molecular Weight (g/mol) | 189.67 | 24.31 | | 47.87 |
| Moles | 5.27 | 8.23 | | 4.11 |
| Stoichiometric Coefficients | 1 | 2 | | 1 |
| Stoichiometric Equivalents | 5.27 | 4.11 | | 4.11 |

As you learned in Chapter 1 , density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 12 demonstrates.

### Example 3.4.1

Ethyl acetate ($CH_3CO_2C_2H_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol ($C_2H_5OH$) with acetic acid ($CH_3CO_2H$); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.




**Given:** reactants, products, and volumes and densities of reactants

**Asked for:** mass of product

**Strategy:**

**A** Balance the chemical equation for the reaction.

**B** Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.

**C** Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.

**D** Convert from moles of product to mass of product.

**Solution**

**A** We always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH\,(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O\,(l)$$

**B** We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall from Chapter 1 " that the density of a substance is the mass divided by the volume:

$$density = \frac{mass}{volume}$$

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 $cm^3$):

$$\begin{aligned} moles\ C_2H_5OH &= \frac{mass\ C_2H_5OH}{molar\ mass\ C_2H_5OH} \\ &= \frac{volume\ C_2H_5OH \times density\ C_2H_5OH}{molar\ mass\ C_2H_5OH} \\ &= 100.0\ \cancel{mL\ C_2H_5OH} \times \frac{0.789\ \cancel{g\ C_2H_5OH}}{1\ \cancel{mL\ C_2H_5OH}} \frac{1\ mol\ mL\ C_2H_5OH}{46.07\ \cancel{g\ C_2H_5OH}} \\ &= 0.171\ mol\ C_2H_5OH \end{aligned}$$

and

$$\begin{aligned} moles\ CH_3CO_2H &= \frac{mass\ CH_3CO_2H}{molar\ mass\ CH_3CO_2H} \\ &= \frac{volume\ CH_3CO_2H \times density\ CH_3CO_2H}{molar\ mass\ CH_3CO_2H} \\ &= 10.0\ \cancel{mL\ CH_3CO_2H} \times \frac{1.0492\ \cancel{g\ CH_3CO_2H}}{1\ \cancel{mL\ CH_3CO_2H}} \frac{1\ mol\ mL\ CH_3CO_2H}{60.05\ \cancel{g\ CH_3CO_2H}} \\ &= 0.175\ mol\ CH_3CO_2H \end{aligned}$$

**C** The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned} moles\ ethyl\ acetate &= mol\ ethanol \times \frac{1\ mol\ ethyl\ acetate}{1\ mol\ ethanol} \\ &= 0.171\ \cancel{mol\ ethanol} \times \frac{1\ mol\ ethyl\ acetate}{1\ \cancel{mol\ ethanol}} \\ &= 0.171\ mol\ CH_3CO_2C_2H_5 \end{aligned}$$

**D** The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned} mass\ of\ ethyl\ acetate &= mol\ ethyl\ acetate \times molar\ mass\ ethyl\ acetate \\ &= 0.171\ \cancel{mol\ CH_3CO_2C_2H_5} \times \frac{88.1\ g\ CH_3CO_2C_2H_5}{1\ \cancel{mol\ CH_3CO_2C_2H_5}} \\ &= 15.1\ g\ CH_3CO_2C_2H_5 \end{aligned}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm$^3$) to determine the volume of ethyl acetate that could be produced:

$$\begin{aligned} volume\ of\ ethyl\ acetate &= 15.1\ g\ CH_3CO_2C_2H_5 \times \frac{1\ mL CH_3CO_2C_2H_5}{0.9003\ \cancel{g\ CH_3CO_2C_2H_5}} \\ &= 16.8\ mL\ CH_3CO_2C_2H_5 \end{aligned}$$

**? Exercise 3.4.1**

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound $P_4S_{10}$. How much $P_4S_{10}$ can be prepared starting with 10.0 g of $P_4$ and 30.0 g of $S_8$?

**Answer**

35.9 g

## Percent Yield

You have learned that when reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, which is the maximum amount of product that can be formed from the reactants in a chemical reaction, which theoretically is the amount of product that would be obtained if the reaction occurred perfectly and the method of purifying the product were 100% efficient. The amount you would obtain if the reaction occurred perfectly and your method of purifying the product were 100% efficient.

In reality, you almost always obtain less product than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not go all the way to completion, thus resulting in a mixture of products and reactants. This last possibility is a common occurrence, which we call a chemical equilibrium. This is not a static equilibrium where two people are standing holding three balls, but a situation where the rate of forward reaction is balanced by the rate of reverse reaction. You could think of this as jugglers tossing the balls back and forth. So the actual yield (the measured mass of products actually obtained from a reaction). The actual yield is nearly always less than the theoretical yield., the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield (the ratio of the actual yield of a reaction to the theoretical yield multiplied by 100 to give a percentage) of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$percent\ yield = \frac{actual yield\,(g)}{theoretical\ yield\,(g)} \times 100 \tag{3.4.4}$$

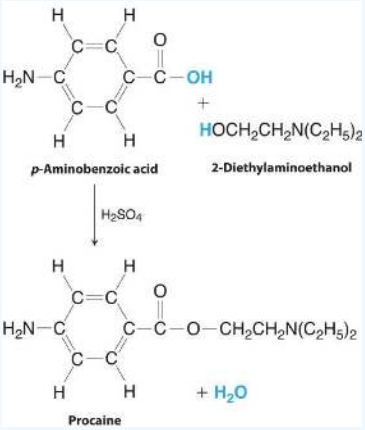
The method used to calculate the percent yield of a reaction is illustrated in Example 13.

**✓ Example 3.4.1**

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of $H_2SO_4$ (indicated above the arrow) by the reaction

$$\underset{p-aminobenzonic\ acid}{C_7H_7NO_2} + \underset{2-diethylaminoethanol}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{procaine}{C_{13}H_{20}N_2O_2} + H_2O$$

If we carried out this reaction using 10.0 g of *p*-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and we isolated 15.7 g of procaine, what was the percent yield?




**The preparation of procaine.** A reaction of *p*-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

**Given:** masses of reactants and product

**Asked for:** percent yield

**Strategy:**

**A** Write the balanced chemical equation.

**B** Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.

**C** Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

**Solution**

**A** From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

**B** To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: *p*-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$moles\ p-aminobenzoic\ acid \quad = \quad 10.0\ \cancel{g}\frac{1\ mol}{137.14\ \cancel{g}} \quad = \quad 0.0729\ mol\ p-ABA$$

$$moles\ 2-diethylaminoethanol \quad = \quad 10.0\ \cancel{g}\frac{1\ mol}{117.19\ \cancel{g}} \quad = \quad 0.0853\ mol\ 2-dAE$$

The reaction requires a 1:1 mole ratio of the two reactants, so *p*-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of *p*-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula ($C_{13}H_{20}N_2O_2$) to calculate its molar mass, which is 236.31 g/mol.

$$theoretical\ yield\ of\ procaine = 0.0729\ \cancel{mol} \times \frac{236.31\ g}{1\ \cancel{mol}} = 17.2\ g$$

**C** The actual yield was only 15.7 g of procaine, so the percent yield was

$$percent\ yield = \frac{15.7\ g}{17.2\ g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate that we have very good lab technique!)

**? Exercise 3.4.1**

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

$$2PbS\,(s) + 3O_2\,(g) \rightarrow 2PbO\,(s) + 2SO_2\,(g)$$

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$PbO\,(s) + C\,(s) \rightarrow Pb\,(l) + CO\,(g)$$

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?

***Crystalline galena (a) and a sample of lead (b).*** *Pure lead is soft enough to be shaped easily with a hammer, unlike the brittle mineral galena, the main ore of lead.*

**Answer**

89.2%

Percent yield can range from 0% to 100%.In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student *must* have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments! A 100% yield means that everything worked perfectly, and you obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows how unlikely a 100% yield is. At the other extreme, a yield of 0% means that *no* product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

## Summary

The **stoichiometry** of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A **stoichiometric quantity** of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is *in excess*. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the **limiting reactant**. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the **theoretical yield** of the reaction. The **actual yield** is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The **percent yield** of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

## Key Takeaway

- The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained.

## Conceptual Problems

1. Engineers use conservation of mass, called a "mass balance," to determine the amount of product that can be obtained from a chemical reaction. Mass balance assumes that the total mass of reactants is equal to the total mass of products. Is this a chemically valid practice? Explain your answer.

2. Given the equation $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$, is it correct to say that 10 g of hydrogen will react with 10 g of oxygen to produce 20 g of water vapor?
3. What does it mean to say that a reaction is *stoichiometric*?
4. When sulfur is burned in air to produce sulfur dioxide, what is the limiting reactant? Explain your answer.
5. Is it possible for the percent yield to be greater than the theoretical yield? Justify your answer.

### Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 7.7) before proceeding to the Numerical Problems.*

1. What is the formula mass of each species?
    1. ammonium chloride
    2. sodium cyanide
    3. magnesium hydroxide
    4. calcium phosphate
    5. lithium carbonate
    6. hydrogen sulfite ion
2. What is the molecular or formula mass of each compound?
    1. potassium permanganate
    2. sodium sulfate
    3. hydrogen cyanide
    4. potassium thiocyanate
    5. ammonium oxalate
    6. lithium acetate
3. How many moles are in each of the following?
    1. 10.76 g of Si
    2. 8.6 g of Pb
    3. 2.49 g of Mg
    4. 0.94 g of La
    5. 2.68 g of chlorine gas
    6. 0.089 g of As
4. How many moles are in each of the following?
    1. 8.6 g of $CO_2$
    2. 2.7 g of CaO
    3. 0.89 g of KCl
    4. 4.3 g of $SrBr_2$
    5. 2.5 g of NaOH
    6. 1.87 g of $Ca(OH)_2$
5. Convert the following to moles and millimoles.
    1. 1.68 g of $Ba(OH)_2$
    2. 0.792 g of $H_3PO_4$
    3. 3.21 g of $K_2S$
    4. 0.8692 g of $Cu(NO_3)_2$
    5. 10.648 g of $Ba_3(PO_4)_2$
    6. 5.79 g of $(NH_4)_2SO_4$
    7. 1.32 g of $Pb(C_2H_3O_2)_2$

8. 4.29 g of $CaCl_2 \cdot 6H_2O$

6. Convert the following to moles and millimoles.

    1. 0.089 g of silver nitrate
    2. 1.62 g of aluminum chloride
    3. 2.37 g of calcium carbonate
    4. 1.004 g of iron(II) sulfide
    5. 2.12 g of dinitrogen pentoxide
    6. 2.68 g of lead(II) nitrate
    7. 3.02 g of ammonium phosphate
    8. 5.852 g of sulfuric acid
    9. 4.735 g of potassium dichromate

7. What is the mass of each substance in grams and milligrams?

    1. 5.68 mol of Ag
    2. 2.49 mol of Sn
    3. 0.0873 mol of Os
    4. 1.74 mol of Si
    5. 0.379 mol of $H_2$
    6. 1.009 mol of Zr

8. What is the mass of each substance in grams and milligrams?

    1. 2.080 mol of $CH_3OH$
    2. 0.288 mol of $P_4$
    3. 3.89 mol of $ZnCl_2$
    4. 1.800 mol of $Fe(CO)_5$
    5. 0.798 mol of $S_8$
    6. 4.01 mol of NaOH

9. What is the mass of each compound in kilograms?

    1. 6.38 mol of $P_4O_{10}$
    2. 2.26 mol of $Ba(OH)_2$
    3. 4.35 mol of $K_3PO_4$
    4. 2.03 mol of $Ni(ClO_3)_2$
    5. 1.47 mol of $NH_4NO_3$
    6. 0.445 mol of $Co(NO_3)_3$

10. How many atoms are contained in each?

    1. 2.32 mol of Bi
    2. 0.066 mol of V
    3. 0.267 mol of Ru
    4. 4.87 mol of C
    5. 2.74 g of $I_2$
    6. 1.96 g of Cs
    7. 7.78 g of $O_2$

11. Convert each number of atoms to milligrams.

    1. $5.89 \times 10^{22}$ Pt atoms
    2. $2.899 \times 10^{21}$ Hg atoms
    3. $4.826 \times 10^{22}$ atoms of chlorine

12. Write a balanced chemical equation for each reaction and then determine which reactant is in excess.

1. 2.46 g barium(s) plus 3.89 g bromine(l) in water to give barium bromide
2. 1.44 g bromine(l) plus 2.42 g potassium iodide(s) in water to give potassium bromide and iodine
3. 1.852 g of Zn metal plus 3.62 g of sulfuric acid in water to give zinc sulfate and hydrogen gas
4. 0.147 g of iron metal reacts with 0.924 g of silver acetate in water to give iron(II) acetate and silver metal
5. 3.142 g of ammonium phosphate reacts with 1.648 g of barium hydroxide in water to give ammonium hydroxide and barium phosphate

13. Under the proper conditions, ammonia and oxygen will react to form dinitrogen monoxide (nitrous oxide, also called laughing gas) and water. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.
    1. 24.6 g of ammonia and 21.4 g of oxygen
    2. 3.8 mol of ammonia and 84.2 g of oxygen
    3. $3.6 \times 10^{24}$ molecules of ammonia and 318 g of oxygen
    4. 2.1 mol of ammonia and 36.4 g of oxygen
14. When a piece of zinc metal is placed in aqueous hydrochloric acid, zinc chloride is produced, and hydrogen gas is evolved. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.
    1. 12.5 g of HCl and 7.3 g of Zn
    2. 6.2 mol of HCl and 100 g of Zn
    3. $2.1 \times 10^{23}$ molecules of Zn and 26.0 g of HCl
    4. 3.1 mol of Zn and 97.4 g of HCl
15. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.
    1. $NaI(aq) + Cl_2(g) \rightarrow NaCl(aq) + I_2(s)$; 1.0 mol of NaCl
    2. $NaCl(aq) + H_2SO_4(aq) \rightarrow HCl(g) + Na_2SO_4(aq)$; 0.50 mol of HCl
    3. $NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$; 1.5 mol of $HNO_3$
16. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.
    1. $AgNO_3(aq) + CaCl_2(s) \rightarrow AgCl(s) + Ca(NO_3)_2(aq)$; 1.25 mol of AgCl
    2. $Pb(s) + PbO_2(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2O(l)$; 3.8 g of $PbSO_4$
    3. $H_3PO_4(aq) + MgCO_3(s) \rightarrow Mg_3(PO_4)_2(s) + CO_2(g) + H_2O(l)$; 6.41 g of $Mg_3(PO_4)_2$
17. Determine the percent yield of each reaction. Be sure that the chemical equations are balanced. Assume that any reactants for which amounts are not given are in excess. (The symbol Δ indicates that the reactants are heated.)
    1. For $KClO_3(s) \rightarrow KCl(s) + O_2(g)$ ,2.14 g of $KClO_3$ produces 0.67 g of $O_2$
    2. $Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + H_2O(l)$; 4.00 g of copper gives 1.2 g of sulfur dioxide
    3. $AgC_2H_3O_2(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + NaC_2H_3O_2(aq)$; 5.298 g of silver acetate produces 1.583 g of silver phosphate
18. Each step of a four-step reaction has a yield of 95%. What is the percent yield for the overall reaction?
19. A three-step reaction yields of 87% for the first step, 94% for the second, and 55% for the third. What is the percent yield of the overall reaction?
20. Give a general expression relating the theoretical yield (in grams) of product that can be obtained from *x* grams of B, assuming neither A nor B is limiting.

$$A + 3B \rightarrow 2C$$

21. Under certain conditions, the reaction of hydrogen with carbon monoxide can produce methanol.
    1. Write a balanced chemical equation for this reaction.

2. Calculate the percent yield if exactly 200 g of methanol is produced from exactly 300 g of carbon monoxide.

22. Chlorine dioxide is a bleaching agent used in the paper industry. It can be prepared by the following reaction:

$$NaClO_2\,(s) + Cl_2\,(g) \rightarrow ClO_2(aq) + NaCl(aq)$$

    1. What mass of chlorine is needed for the complete reaction of 30.5 g of $NaClO_2$?
    2. Give a general equation for the conversion of *x* grams of sodium chlorite to chlorine dioxide.

23. The reaction of propane gas ($CH_3CH_2CH_3$) with chlorine gas ($Cl_2$) produces two monochloride products: $CH_3CH_2CH_2Cl$ and $CH_3CHClCH_3$. The first is obtained in a 43% yield and the second in a 57% yield.

    1. If you use 2.78 g of propane gas, how much chlorine gas would you need for the reaction to go to completion?
    2. How many grams of each product could theoretically be obtained from the reaction starting with 2.78 g of propane?
    3. Use the actual percent yield to calculate how many grams of each product would actually be obtained.

24. Protactinium (Pa), a highly toxic metal, is one of the rarest and most expensive elements. The following reaction is one method for preparing protactinium metal under relatively extreme conditions:

$$2PaI_5\,(s) \xrightarrow{\Delta} 2Pa\,(s) + 5I_2\,(s)$$

    1. Given 15.8 mg of reactant, how many milligrams of protactinium could be synthesized?
    2. If 3.4 mg of Pa was obtained, what was the percent yield of this reaction?
    3. If you obtained 3.4 mg of Pa and the percent yield was 78.6%, how many grams of $PaI_5$ were used in the preparation?

25. Aniline ($C_6H_5NH_2$) can be produced from chlorobenzene ($C_6H_5Cl$) via the following reaction:

$$C_6H_5Cl\,(l) + 2NH_3\,(g) \rightarrow C_6H_5NH_2\,(l) + NH_4Cl\,(s)$$

    Assume that 20.0 g of chlorobenzene at 92% purity is mixed with 8.30 g of ammonia.

    1. Which is the limiting reactant?
    2. Which reactant is present in excess?
    3. What is the theoretical yield of ammonium chloride in grams?
    4. If 4.78 g of $NH_4Cl$ was recovered, what was the percent yield?
    5. Derive a general expression for the theoretical yield of ammonium chloride in terms of grams of chlorobenzene reactant, if ammonia is present in excess.

26. A stoichiometric quantity of chlorine gas is added to an aqueous solution of NaBr to produce an aqueous solution of sodium chloride and liquid bromine. Write the chemical equation for this reaction. Then assume an 89% yield and calculate the mass of chlorine given the following:

    1. $9.36 \times 10^{24}$ formula units of NaCl
    2. $8.5 \times 10^{4}$ mol of $Br_2$
    3. $3.7 \times 10^{8}$ g of NaCl

## Answers

1. 1. 53.941 amu
    2. 49.0072 amu
    3. 58.3197 amu
    4. 310.177 amu
    5. 73.891 amu
    6. 81.071 amu
2.

3. 1. 0.3831 mol Si
   2. $4.2 \times 10^{-2}$ mol Pb
   3. 0.102 mol Mg
   4. $6.8 \times 10^{-3}$ mol La
   5. $3.78 \times 10^{-2}$ mol $Cl_2$
   6. $1.2 \times 10^{-3}$ mol As
4. 
5. 1. $9.80 \times 10^{-3}$ mol or 9.80 mmole $Ba(OH)_2$
   2. $8.08 \times 10^{-3}$ mol or 8.08 mmole $H_3PO_4$
   3. $2.91 \times 10^{-2}$ mol or 29.1 mmole $K_2S$
   4. $4.634 \times 10^{-3}$ mol or 4.634 mmole $Cu(NO_3)_2$
   5. $1.769 \times 10^{-2}$ mol 17.69 mmole $Ba_3(PO_4)_2$
   6. $4.38 \times 10^{-2}$ mol or 43.8 mmole $(NH_4)_2SO_4$
   7. $4.06 \times 10^{-3}$ mol or 4.06 mmole $Pb(C_2H_3O_2)_2$
   8. $1.96 \times 10^{-2}$ mol or 19.6 mmole $CaCl_2 \cdot 6H_2O$
6. 
7. 1. 613 g or $6.13 \times 10^5$ mg Ag
   2. 296 g or $2.96 \times 10^5$ mg Sn
   3. 16.6 g or $1.66 \times 10^4$ mg Os
   4. 48.9 g or $4.89 \times 10^4$ mg Si
   5. 0.764 g or 764 mg $H_2$
   6. 92.05 g or $9.205 \times 10^4$ mg Zr
8. 
9. 1. 1.81 kg $P_4O_{10}$
   2. 0.387 kg $Ba(OH)_2$
   3. 0.923 kg $K_3PO_4$
   4. 0.458 kg $Ni(ClO_3)_2$
   5. 0.118 kg $(NH_4)NO_3$
   6. 0.109 kg $Co(NO_3)_3$
10. 
11. 1. $1.91 \times 10^4$ mg Pt
    2. 965.6 mg Hg
    3. 2841 mg Cl
12. 
13. The balanced chemical equation for this reaction is

    $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

    1. $NH_3$
    2. $NH_3$
    3. $O_2$
    4. $NH_3$
14. 
15. 1. 150 g NaI and 35 g $Cl_2$
    2. 29 g NaCl and 25 g $H_2SO_4$
    3. 140 g $NO_2$ and 27 g $H_2O$
16. 
17. 1. 80%

2. 30%
3. 35.7%

18.

19. 45%.

20.

21. 1. $CO + 2H_2 \rightarrow CH_3OH$
    2. 58.28%

22.

23. 1. 2.24 g $Cl_2$
    2. 4.95 g
    3. 2.13 g $CH_3CH_2CH_2Cl$ plus 2.82 g $CH_3CHClCH_3$

24.

25. 1. chlorobenzene
    2. ammonia
    3. 8.74 g ammonium chloride.
    4. 55%
    5.

26.

## Contributors

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# 3.5: Types of Chemical Reactions

**Learning Objectives**

- To identify fundamental types of chemical reactions.
- To predict the types of reactions substances will undergo.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types: acid–base reactionsA reaction of the general form acid + base → salt., exchange reactionsA chemical reaction that has the general form AB + C → AC + B or AB + CD → AD + CB., condensation reactionsA chemical reaction that has the general form A + B → AB. Condensation reactions are the reverse of cleavage reactions. Some, but not all, condensation reactions are also oxidation–reduction reactions. (and the reverse, cleavage reactionsA chemical reaction that has the general form AB → A + B. Cleavage reactions are the reverse of condensation reactions.), and oxidation–reduction reactionsA chemical reaction that exhibits a change in the oxidation states of one or more elements in the reactants that has the general form oxidant + reductant → reduced oxidant + oxidized reductant.. The general forms of these five kinds of reactions are summarized in Table 3.5.1, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion. The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions and one kind of exchange reaction—the formation of an insoluble salt such as barium sulfate when solutions of two soluble salts are mixed together—will be discussed in Chapter 8 .

**Table 3.5.1 Basic Types of Chemical Reactions**

| Name of Reaction | General Form | Example(s) |
|---|---|---|
| oxidation–reduction (redox) | oxidant + reductant → reduced oxidant + oxidized reductant | $C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$ |
| acid–base | acid + base → salt | $NH_3(aq) + HNO_3(aq) \rightarrow NH_4^+(aq) + NO_3^-(aq)$ |
| exchange | AB + C → AC + B | $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$ |
| | AB + CD → AD + CB | $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$ |
| condensation | A + B → AB | $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ |
| | | $HBr + H_2C{=}CH_2 \rightarrow CH_3CH_2Br$* |
| cleavage | AB → A + B | $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ |
| | | $CH_3CH_2Cl \rightarrow H_2C{=}CH_2 + HCl$** |

* In more advanced chemistry courses you will learn that this reaction is also called an *addition* reaction.

** In more advanced chemistry courses you will learn that this reaction is also called an *elimination* reaction.

## Oxidation–Reduction Reactions

The term oxidation refers to the loss of one or more electrons in a chemical reaction. The substance that loses electrons is said to be oxidized. was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When exposed to air, aluminum metal

develops a continuous, coherent, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions ($O^{2-}$). Because the metals have lost electrons to oxygen, they have been *oxidized*; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been *reduced*, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction.

### Note the Pattern

Any oxidation *must* be accompanied by a reduction and vice versa.

The term reduction refers to the gain of one or more electrons in a chemical reaction. The substance that gains electrons is said to be reduced. referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water). The reaction is as follows:

$$Cu_2O\,(s) + H_2\,(g) \rightarrow 2Cu\,(s) + H_2O\,(g)$$

Oxidation and reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants, which follows the mnemonic *oxidation is loss reduction is gain*, or *oil rig*. The oxidation state: The charge that each atom in a compound would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as $O_2$ or $H_2$, are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is

$$4Al\,(s) + 3O_2\,(g) \rightarrow 2Al_2O_3\,(s)$$

Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of −2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of +3 in the product, so aluminum has been oxidized. In the formation of $Al_2O_3$, electrons are transferred as follows (the superscript 0 emphasizes the oxidation state of the elements):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^{+}6O^{2-}$$

Equation 3.5.1 and Equation 3.5.2 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must equal the total of electrons gained to preserve electrical neutrality. In Equation 3.5.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned} electrons\ lost &= 4\ \cancel{Al\ atoms} \times \frac{3\ e^-\ lost}{\cancel{Al\ atoms}} = 12\ e^-\ lost \\ electrons\ gained &= 6\ \cancel{O\ atoms} \times \frac{2\ e^-\ gained}{\cancel{O\ atoms}} = 12\ e^-\ gained \end{aligned} \tag{3.5.1}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained.

### Note the Pattern

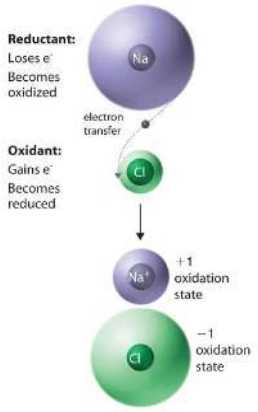
In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.

## Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. In Chapter 5, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 3.5.1, magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds can be understood in terms of polar covalent bonds and

electronegativity. Oxidation states assume that electrons are completely transferred. While this is not true, it is almost true, and the oxidation state model can help you understand and predict many reactions. For example, in water, the oxidation state of the oxygen atom is -2 and that of each hydrogen is +1. That is the oxidation state model assumes that the hydrogen atoms transfer an electron completely to the oxygen atom. We know this is not the case, but that the electrons from the hydrogen atoms are found closter to the oxygen atom. A more extreme case is carbon dioxide, where the oxidation states of the more electronegative oxygen atoms are -2 and that of the carbon atom is +4. Again, the idea is that the oxidation state model assumes complete transfer, and the atomic bond model tell us that the transfer is only partial. Still, the oxidation state model is useful as we shall see

**Figure** 3.5.1 **The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom**




The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

A set of rules for assigning oxidation states to atoms in chemical compounds follows.

## Rules for Assigning Oxidation States:

1. The oxidation state of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation state of a monatomic ion is the same as its charge—for example, $Na^+ = +1$, $Cl^- = -1$.
3. The oxidation state of fluorine in chemical compounds is always −1. Other halogens usually have oxidation states of −1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of +1 in its compounds with nonmetals and −1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of −2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation state of oxygen is determined by the oxidation states of the other elements present.
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl, for example, Na has an oxidation state of +1 and Cl is −1. The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you discovered in Chapter 7 . Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the $H^-$ ion, whereas HCl forms $H^+$ and $Cl^-$ ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in $OF_2$ but −½ in $KO_2$. Note that an oxidation state of −½ for O in $KO_2$ is perfectly acceptable. Nonintegral oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states, so that the "average" oxidation state is a fraction. As with resonance structures, this is a failure of the model.

The reduction of copper(I) oxide shown in Equation 3.5.5 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to $H_2$ and Cu. From rule 4, hydrogen in $H_2O$ has an oxidation state of +1, and from rule 5, oxygen in both $Cu_2O$ and $H_2O$ has an oxidation state of −2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in $Cu_2O$ must have a charge of +1: 2(+1) + (−2) = 0. So the oxidation states are as follows:

$$\overset{+1}{\underset{-2}{Cu_2O}}\,(s) + \overset{0}{H_2} \rightarrow 2\overset{0}{Cu}\,(s) + \overset{+1}{\underset{-2}{H_2O}}\,(g) \tag{3.5.2}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). So this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

$$\begin{aligned} electrons\ lost &= 2\ \cancel{H\ atoms} \times \frac{1\ e^-\ lost}{\cancel{H\ atoms}} = 2\ e^-\ lost \\ electrons\ gained &= 2\ \cancel{Cu\ atoms} \times \frac{1\ e^-\ gained}{\cancel{Cu\ atoms}} = 2\ e^-\ gained \end{aligned} \tag{3.5.3}$$

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation–reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

### Example 3.5.1

Assign oxidation states to all atoms in each compound.

1. sulfur hexafluoride ($SF_6$)
2. methanol ($CH_3OH$)
3. ammonium sulfate [$(NH_4)_2SO_4$]
4. magnetite ($Fe_3O_4$)
5. ethanoic (acetic) acid ($CH_3CO_2H$)

**Given:** molecular or empirical formula

**Asked for:** oxidation states

**Strategy:**

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

**Solution:**

1. We know from rule 3 that fluorine always has an oxidation state of −1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of −6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here $SF_6$), the oxidation state of sulfur must be +6: [(6 F atoms)(−1)] + [(1 S atom) (+6)] = 0
2. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and −2, respectively. Because methanol has no net charge, carbon must have an oxidation state of −2: [(4 H atoms)(+1)] + [(1 O atom)(−2)] + [(1 C atom)(−2)] = 0
3. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation ($NH_4^+$) and a polyatomic anion ($SO_4^{2-}$) (see Table 6.2.1 ). We assign oxidation states to the atoms in each polyatomic ion separately. For $NH_4^+$, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of −3: [(4 H atoms)(+1)] + [(1 N atom)(−3)] = +1, the charge on the $NH_4^+$ ion

   For $SO_4^{2-}$, oxygen has an oxidation state of −2 (rule 5), so sulfur must have an oxidation state of +6:

   [(4 O atoms) (−2)] + [(1 S atom)(+6)] = −2, the charge on the sulfate ion
4. Oxygen has an oxidation state of −2 (rule 5), giving an overall charge of −8 per formula unit. This must be balanced by the positive charge on three iron atoms, giving an oxidation state of +8/3 for iron:

Fractional oxidation states are allowed because oxidation states are a somewhat arbitrary way of keeping track of electrons. In fact, $Fe_3O_4$ can be viewed as having two $Fe^{3+}$ ions and one $Fe^{2+}$ ion per formula unit, giving a net positive charge of +8 per formula unit. $Fe_3O_4$ is a magnetic iron ore commonly called magnetite. In ancient times, magnetite was known as lodestone because it could be used to make primitive compasses that pointed toward Polaris (the North Star), which was called the "lodestar."

5. Initially, we assign oxidation states to the components of $CH_3CO_2H$ in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and −2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of [

$$(4Hatoms)(+1)] + [(2Oatoms)(-2)] = 0 \tag{3.5.4}$$

So the oxidation state of carbon must also be zero (rule 6). This is, however, an *average* oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($-CH_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of −3. Similarly, the carbon atom of the carboxylic acid group ($-CO_2H$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of −2 and +1 to the oxygen and hydrogen atoms, respectively, leading to a net charge of

[(2 O atoms)(−2)] + [(1 H atom)(+1)] = −3

To obtain an electrically neutral carboxylic acid group, the charge on this carbon must be +3. The oxidation states of the individual atoms in acetic acid are thus

$$\overset{+1}{\underset{-3}{C}}\overset{+1}{H_3}\overset{+3}{\underset{-2}{C}}\overset{+1}{O_2H} \tag{3.5.5}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

**? Exercise 3.5.1**

Assign oxidation states to all atoms in each compound.

1. barium fluoride ($BaF_2$)
2. formaldehyde ($CH_2O$)
3. potassium dichromate ($K_2Cr_2O_7$)
4. cesium oxide ($CsO_2$)
5. ethanol ($CH_3CH_2OH$)

**Answer**

1. Ba, +2; F, −1
2. C, 0; H, +1; O, −2
3. K, +1; Cr, +6; O, −2
4. Cs, +1; O, −½
5. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

## Oxidants and Reductants

Compounds that are capable of accepting electrons, such as $O_2$ or $F_2$, are called oxidants (or oxidizing agents)A compound that is capable of accepting electrons; thus it is reduced. because they can oxidize other compounds. *In the process of accepting electrons, an oxidant is reduced.* Compounds that are capable of donating electrons, such as sodium metal or cyclohexane ($C_6H_{12}$), are called

reductants (or reducing agents)A compound that is capable of donating electrons; thus it is oxidized. because they can cause the reduction of another compound. *In the process of donating electrons, a reductant is oxidized.* These relationships are summarized in Equation 7.5.7:

$$oxidant + reductant \rightarrow oxidation - reduction \tag{3.5.6}$$

$$\underset{gains\ e^-}{\overset{(is\ reduced)}{O_2}}\ (g) + \underset{loses\ e^-}{\overset{(is\ oxidized)}{4Na}}\ (s) \rightarrow \underset{redox\ reaction}{2Na_2O} \tag{7.5.7}$$

Some oxidants have a greater ability than others to remove electrons from other compounds. Oxidants can range from very powerful, capable of oxidizing most compounds with which they come in contact, to rather weak. Both $F_2$ and $Cl_2$ are powerful oxidants: for example, $F_2$ will oxidize $H_2O$ in a vigorous, potentially explosive reaction. In contrast, $S_8$ is a rather weak oxidant, and $O_2$ falls somewhere in between. Conversely, reductants vary in their tendency to donate electrons to other compounds. Reductants can also range from very powerful, capable of giving up electrons to almost anything, to weak. The alkali metals are powerful reductants, so they must be kept away from atmospheric oxygen to avoid a potentially hazardous redox reaction.

A combustion reactionAn oxidation–reduction reaction in which the oxidant is .$O_2$, first introduced in Section 7.2 is an oxidation–reduction reaction in which the oxidant is $O_2$. One example of a combustion reaction is the burning of a candle, shown in Figure 7.3.3 . Consider, for example, the combustion of cyclohexane, a typical hydrocarbon, in excess oxygen. The balanced chemical equation for the reaction, with the oxidation state shown for each atom, is as follows:

$$\underset{-2}{\overset{+1}{C_6H_{12}}} + \overset{0}{O_2} \rightarrow \underset{-2}{\overset{+4}{CO_2}} + 6\underset{-2}{\overset{+1}{H_2O}} \tag{7.5.8}$$

If we compare the oxidation state of each element in the products and the reactants, we see that hydrogen is the only element whose oxidation state does not change; it remains +1. Carbon, however, has an oxidation state of −2 in cyclohexane and +4 in $CO_2$; that is, each carbon atom changes its oxidation state by six electrons during the reaction. Oxygen has an oxidation state of 0 in the reactants, but it gains electrons to have an oxidation state of −2 in $CO_2$ and $H_2O$. Because carbon has been oxidized, cyclohexane is the reductant; because oxygen has been reduced, it is the oxidant. All combustion reactions are therefore oxidation–reduction reactions.

## Condensation Reactions

The reaction of bromine with ethylene to give 1,2-dibromoethane, which is used in agriculture to kill nematodes in soil, is as follows:

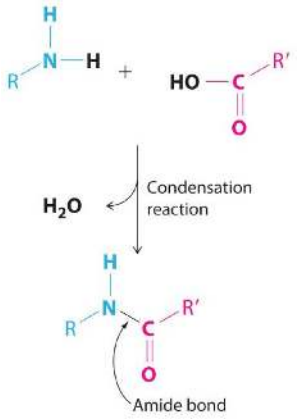
$$C_2H_4\,(g) + Br_2\,(g) \rightarrow BrCH_2CH_2Br\,(g) \tag{7.5.9}$$

According to Table 7.1.1, this is a condensation reaction because it has the general form A + B → AB. This reaction, however, can also be viewed as an oxidation–reduction reaction, in which electrons are transferred from carbon (−2 → −1) to bromine (0 → −1). Another example of a condensation reaction is the one used for the industrial synthesis of ammonia:

$$3H_2\,(g) + N_2\,(g) \rightarrow 2NH_3\,(g) \tag{7.5.10}$$

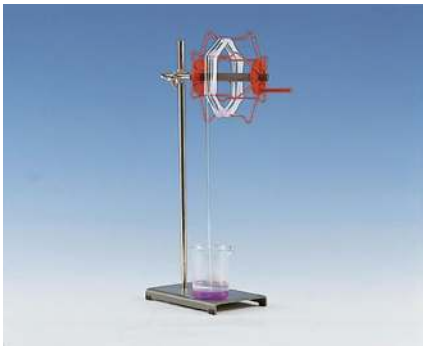
Although this reaction also has the general form of a condensation reaction, hydrogen has been oxidized (0 → +1) and nitrogen has been reduced (0 → −3), so it can also be classified as an oxidation–reduction reaction.

Not all condensation reactions are redox reactions. The reaction of an amine with a carboxylic acid, for example, is a variant of a condensation reaction (A + B → A′B′ + C): two large fragments condense to form a single molecule, and a much smaller molecule, such as $H_2O$, is eliminated. In this reaction, the −OH from the carboxylic acid group and −H from the amine group are eliminated as $H_2O$, and the reaction forms an *amide bond* (also called a *peptide bond*) that links the two fragments. Amide bonds are the essential structural unit linking the building blocks of proteins and many polymers together. Nylon, for example, is produced from a condensation reaction (Figure 7.5.2 ).




**Amide bonds.** The reaction of an amine with a carboxylic acid proceeds by eliminating water and forms a new C–N (amide) bond.

**Figure 7.5.2 The Production of Nylon**



Example 3.5.2

The following reactions have important industrial applications. Using Table 3.5.1, classify each reaction as an oxidation–reduction reaction, an acid–base reaction, an exchange reaction, a condensation reaction, or a cleavage reaction. For each redox reaction, identify the oxidant and reductant and specify which atoms are oxidized or reduced. (Don't forget that some reactions can be placed into more than one category.)

1. $C_2H_4(g) + Cl_2(g) \rightarrow ClCH_2CH_2Cl(g)$
2. $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
3. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
4. $Ca_5(PO_4)_3(OH)(s) + 7H_3PO_4(aq) + 4H_2O(l) \rightarrow 5Ca(H_2PO_4)_2{\cdot}H_2O(s)$
5. $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

**Given:** balanced chemical equation

**Asked for:** classification of chemical reaction

**Strategy:**

**A** Determine the general form of the equation by referring to Table 3.5.1 and then classify the reaction.

**B** For redox reactions, assign oxidation states to each atom present in the reactants and the products. If the oxidation state of one or more atoms changes, then the reaction is a redox reaction. If not, the reaction must be one of the other types of reaction listed in Table 3.5.1

**Solution**

1. **A** This reaction is used to prepare 1,2-dichloroethane, one of the top 25 industrial chemicals It has the general form A + B → AB, which is typical of a condensation reaction. **B** Because reactions may fit into more than one category, we need to look at the oxidation states of the atoms:

$$\overset{\ }{\underset{-2}{C_2}}\overset{+1}{H_4} + \overset{0}{Cl_2} \rightarrow \underset{-1}{Cl}\underset{-1}{C}\overset{+1}{H_2}\underset{-1}{Cl}$$

The oxidation states show that chlorine is reduced from 0 to −1 and carbon is oxidized from −2 to −1, so this is a redox reaction as well as a condensation reaction. Ethylene is the reductant, and chlorine is the oxidant.

2. **A** This reaction is used to prepare silver chloride for making photographic film. The chemical equation has the general form AB + CD → AD + CB, so it is classified as an exchange reaction. **B** The oxidation states of the atoms are as follows

$$\overset{+1}{Ag}\overset{+5}{\underset{-2}{N}}\underset{-2}{O_3} + \overset{+1}{Na}\underset{-1}{Cl} \rightarrow \overset{+1}{Ag}\underset{-1}{Cl} + \overset{+1}{Na}\overset{+5}{\underset{-2}{N}}\underset{-2}{O_3}$$

There is no change in the oxidation states, so this is not a redox reaction.

***AgCl(s) precipitates when solutions of $AgNO_3$(aq) and NaCl(aq) are mixed.*** *$NaNO_3$ (aq) is in solution as $Na^+$ and $NO_3^-$ ions*.

3. **A** This reaction is used to prepare lime (CaO) from limestone ($CaCO_3$) and has the general form AB → A + B. The chemical equation's general form indicates that it can be classified as a cleavage reaction, the reverse of a condensation reaction. **B** The oxidation states of the atoms are as follows:

$$\overset{+2}{Ca}\overset{+4}{C}\underset{-2}{O_3} \rightarrow \overset{+2}{Ca}\underset{-2}{O_2} + \overset{+4}{C}\underset{-2}{O_2}$$

>

Because the oxidation states of all the atoms are the same in the products and the reactant, this is *not* a redox reaction.

4. **A** This reaction is used to prepare "super triple phosphate" in fertilizer. One of the reactants is phosphoric acid, which transfers a proton ($H^+$) to the phosphate and hydroxide ions of hydroxyapatite [$Ca_5(PO_4)_3(OH)$] to form $H_2PO_4^-$ and $H_2O$, respectively. This is an acid–base reaction, in which $H_3PO_4$ is the acid ($H^+$ donor) and $Ca_5(PO_4)_3(OH)$ is the base ($H^+$ acceptor).

**B** To determine whether it is also a redox reaction, we assign oxidation states to the atoms:

$$\overset{+2}{Ca_5}\left(\overset{+5}{\underset{-2}{P}}\underset{-2}{O_4}\right)_3\left(\underset{-2}{\overset{+1}{O}}\overset{+1}{H}\right) + 7\overset{+1}{H_3}\overset{+5}{\underset{-2}{P}}\underset{-2}{O_4} \rightarrow 5\overset{+2}{Ca}\left(\overset{+1}{H_2}\overset{+5}{\underset{-2}{P}}\underset{-2}{O_4}\right)_2 \cdot \overset{+1}{\underset{-2}{H_2O}}$$

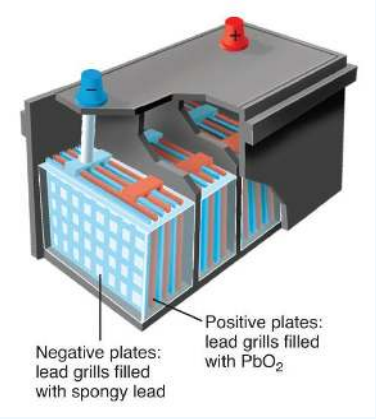
Because there is no change in oxidation state, this is not a redox reaction.

5. **A** This reaction occurs in a conventional car battery every time the engine is started. An acid ($H_2SO_4$) is present and transfers protons to oxygen in $PbO_2$ to form water during the reaction. The reaction can therefore be described as an acid–base reaction.

**B** The oxidation states are as follows:

$$\overset{0}{Pb} + \overset{+4}{\underset{-2}{PbO_2}} + 2\overset{+1}{H_2}\overset{+6}{\underset{-2}{S}}\underset{-2}{O_4} \rightarrow 2\overset{+4}{Pb}\overset{+6}{\underset{-2}{S}}\underset{-2}{O_4} + 2\overset{+1}{\underset{-2}{H_2O}}$$

The oxidation state of lead changes from 0 in Pb and +4 in $PbO_2$ (both reactants) to +2 in $PbSO_4$. This is also a redox reaction, in which elemental lead is the reductant, and $PbO_2$ is the oxidant. Which description is correct? Both.




**Schematic drawing of a 12-volt car battery.** The locations of the reactants (lead metal in a spongy form with large surface area) and $PbO_2$ are shown. The product ($PbSO_4$) forms as a white solid between the plates.

**? Exercise 3.5.2**

Using Table 7.5.1 , classify each reaction as an oxidation–reduction reaction, an acid–base reaction, an exchange reaction, a condensation reaction, or a cleavage reaction. For each redox reaction, identify the oxidant and the reductant and specify which atoms are oxidized or reduced.

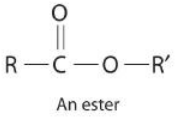
1. $Al(s) + OH^-(aq) + 3H_2O(l) \rightarrow 3/2H_2(g) + [Al(OH)_4]^-(aq)$
2. $TiCl_4(l) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l)$
3. $MgCl_2(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + 2NaCl(aq)$
4. $CO(g) + Cl_2(g) \rightarrow Cl_2CO(l)$
5. $H_2SO_4(l) + 2NH_3(g) \rightarrow (NH_4)_2SO_4(s)$

**Answer**

1. Redox reaction; reductant is Al, oxidant is $H_2O$; Al is oxidized, H is reduced. This is the reaction that occurs when Drano is used to clear a clogged drain.
2. Redox reaction; reductant is Mg, oxidant is $TiCl_4$; Mg is oxidized, Ti is reduced.
3. Exchange reaction. This reaction is responsible for the scale that develops in coffee makers in areas that have hard water.
4. Both a condensation reaction and a redox reaction; reductant is CO, oxidant is $Cl_2$; C is oxidized, Cl is reduced. The product of this reaction is phosgene, a highly toxic gas used as a chemical weapon in World War I. Phosgene is now used to prepare polyurethanes, which are used in foams for bedding and furniture and in a variety of coatings.
5. Acid–base reaction.

## Catalysts

Many chemical reactions, including some of those discussed previously, occur more rapidly in the presence of a catalystA substance that increases the rate of a chemical reaction without undergoing a net chemical change itself., which is a substance that participates in a reaction and causes it to occur more rapidly but can be recovered unchanged at the end of a reaction and reused. Because catalysts are not involved in the stoichiometry of a reaction, they are usually shown above the arrow in a net chemical equation. Chemical processes in industry rely heavily on the use of catalysts, which are usually added to a reaction mixture in trace amounts, and most biological reactions do not take place without a biological catalyst or enzymeCatalysts that occur naturally in living organisms and catalyze biological reactions.. Examples of catalyzed reactions in industry are the use of platinum in petroleum cracking and reforming, the reaction of $SO_2$ and $O_2$ in the presence of $V_2O_5$ to produce $SO_3$ in the industrial synthesis of sulfuric acid, and the use of sulfuric acid in the synthesis of compounds such as ethyl acetate and procaine. Not only do catalysts greatly increase the rates of reactions, but in some cases such as in petroleum refining, they also control which products are formed. The acceleration of a reaction by a catalyst is called catalysisThe acceleration of a chemical reaction by a catalyst..



An ester



**A heterogeneous catalyst.** This large circular gauze, woven from rhodium-platinum wire, is a heterogeneous catalyst in the commercial production of nitric acid by the oxidation of ammonia.

Catalysts may be classified as either homogeneous or heterogeneous. A homogeneous catalystA catalyst that is uniformly dispersed throughout the reactant mixture to form a solution. is uniformly dispersed throughout the reactant mixture to form a solution. Sulfuric acid, for example, is a homogeneous catalyst used in the synthesis of esters such as procaine (Example 13). An ester has a structure similar to that of a carboxylic acid, in which the hydrogen atom attached to oxygen has been replaced by an R group. They are responsible for the fragrances of many fruits, flowers, and perfumes. Other examples of homogeneous catalysts are the enzymes that allow our bodies to function. In contrast, a heterogeneous catalystA catalyst that is in a different physical state than the reactants. is in a different physical state than the reactants. For economic reasons, most industrial processes use heterogeneous catalysts in the form of solids that are added to solutions of the reactants. Because such catalysts often contain expensive precious metals such as platinum or palladium, it makes sense to formulate them as solids that can be easily separated from the liquid or gaseous reactant-product mixture and recovered. Examples of heterogeneous catalysts are the iron oxides used in the industrial synthesis of ammonia and the catalytic converters found in virtually all modern automobiles, which contain precious metals like palladium and rhodium. Catalysis will be discussed in more detail when we discuss reaction rates, in the second semester but you will encounter the term frequently throughout the text.

## Summary

Chemical reactions may be classified as an a**cid–base reaction**, an **exchange reaction**, a **condensation reaction** and its reverse, a **cleavage reaction**, and an **oxidation–reduction (or redox)** reaction. To keep track of electrons in chemical reactions, oxidation states are assigned to atoms in compounds. The **oxidation state** is the charge an atom would have if all its bonding electrons were transferred completely to the atom that has the greater attraction for electrons. In an **oxidation–reduction reaction**, one atom must lose electrons and another must gain electrons. **Oxidation** is the loss of electrons, and an element whose oxidation state increases is said to be *oxidized*. **Reduction** is the gain of electrons, and an element whose oxidation state decreases is said to be *reduced*. **Oxidants** are compounds that are capable of accepting electrons from other compounds, so they are reduced during an oxidation–reduction reaction. In contrast, **reductants** are compounds that are capable of donating electrons to other compounds, so they are oxidized during an oxidation–reduction reaction. A **combustion reaction** is a redox reaction in which the oxidant is $O_2(g)$. An *amide bond* is formed from the condensation reaction between a carboxylic acid and an amine; it is the essential structural unit of proteins and many polymers. A **catalyst** is a substance that increases the rate of a chemical reaction without undergoing a net chemical change itself. A biological catalyst is called an **enzyme**. **Catalysis** is an acceleration in the rate of a reaction caused by the presence of a substance that does not appear in the chemical equation. A **homogeneous catalyst** is uniformly dispersed in a solution of the reactants, whereas a **heterogeneous catalyst** is present as a different phase, usually a solid.

## Key Takeaway

- Chemical reactions may be classified as acid–base, exchange, condensation, cleavage, and oxidation–reduction (redox).

## Conceptual Problems

1. What is a combustion reaction? How can it be distinguished from an exchange reaction?
2. What two products are formed in the combustion of an organic compound containing only carbon, hydrogen, and oxygen? Is it possible to form only these two products from a reaction that is not a combustion reaction? Explain your answer.
3. What factors determine whether a reaction can be classified as a redox reaction?
4. Name three characteristics of a balanced redox reaction.
5. Does an oxidant accept electrons or donate them?
6. Does the oxidation state of a reductant become more positive or more negative during a redox reaction?
7. Nitrogen, hydrogen, and ammonia are known to have existed on primordial earth, yet mixtures of nitrogen and hydrogen do not usually react to give ammonia. What natural phenomenon would have enough energy to initiate a reaction between these two primordial gases?
8. Catalysts are not added to reactions in stoichiometric quantities. Why?
9. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
    1. Platinum metal is used in the catalytic converter of an automobile.
    2. Nitrogen is biologically converted to ammonia by an enzyme.
    3. Carbon monoxide and hydrogen combine to form methane and water with a nickel catalyst.
    4. A dissolved rhodium compound is used as a catalyst for the conversion of an alkene to an alkane.
10. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
    1. Pellets of ZSM-5, an aluminum- and silicon-containing mineral, are used to catalyze the conversion of methanol to gasoline.
    2. The conversion of glucose to a carboxylic acid occurs with catalysis by the enzyme glucose oxidase.
    3. Metallic rhodium is used to the conversion of carbon monoxide and water to carbon dioxide and hydrogen.
11. Complete the following table to describe some key differences between homogeneous and heterogeneous catalysis.

| | Homogeneous | Heterogeneous |
|---|---|---|
| number of phases | | |
| ease of separation from product | | |
| ease of recovery of catalyst | | |

12. To increase the rate of a reaction, a scientist decided to use a catalyst. Unexpectedly, the scientist discovered that the catalyst decreased the yield of the desired product, rather than increasing it. What might have happened?

## Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.

11.

| | Homogeneous | Heterogeneous |
|---|---|---|
| number of phases | single phase | at least two phases |
| ease of separation from product | difficult | easy |
| ease of recovery of catalyst | difficult | easy |

12.

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 7.7 ) before proceeding to the Numerical Problems.*

1. Classify each chemical reaction according to the types listed in Table 7.5.1
    1. $12FeCl_2(s) + 3O_2(g) \rightarrow 8FeCl_3(s) + 2Fe_2O_3(s)$
    2. $CaCl_2(aq) + K_2SO_4(aq) \rightarrow CaSO_4(s) + 2KCl(aq)$
    3. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
    4. $Br_2(l) + C_2H_4(g) \rightarrow BrCH_2CH_2Br(l)$
2. Classify each chemical reaction according to the types listed in Table 7.5.1
    1. $4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$
    2. $Ca_3(PO_4)_2(s) + 3H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$
    3. $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$
    4. ethane(g) + oxygen(g) $\rightarrow$ carbon dioxide(g) + water(g)
3. Assign oxidation states to the atoms in each compound or ion.
    1. $(NH_4)_2S$
    2. the phosphate ion
    3. $[AlF_6]^{3-}$
    4. CuS
    5. $HCO_3^-$
    6. $NH_4^+$
    7. $H_2SO_4$
    8. formic acid
    9. *n*-butanol
4. Assign oxidation states to the atoms in each compound or ion.
    1. $ClO_2$
    2. $HO_2^-$
    3. sodium bicarbonate
    4. $MnO_2$
    5. $PCl_5$
    6. $[Mg(H_2O)_6]^{2+}$
    7. $N_2O_4$
    8. butanoic acid
    9. methanol
5. Balance this chemical equation:

    $NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$

    What type of reaction is this? Justify your answer.
6. Assign oxidation states to the atoms in each compound.

1. iron(III) nitrate
2. $Al_2O_3$
3. potassium sulfate
4. $Cr_2O_3$
5. sodium perchlorate
6. $Cu_2S$
7. hydrazine ($N_2H_4$)
8. $NO_2$
9. *n*-pentanol

7. Assign oxidation states to the atoms in each compound.

    1. calcium carbonate
    2. NaCl
    3. $CO_2$
    4. potassium dichromate
    5. $KMnO_4$
    6. ferric oxide
    7. $Cu(OH)_2$
    8. $Na_2SO_4$
    9. *n*-hexanol

8. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.

    1. $H_2(g) + I_2(s) \rightarrow 2HI(g)$
    2. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
    3. $2F_2(g) + 2NaOH(aq) \rightarrow OF_2(g) + 2NaF(aq) + H_2O(l)$

9. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.

    1. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
    2. $SiCl_4(l) + 2Mg(s) \rightarrow 2MgCl_2(s) + Si(s)$
    3. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

10. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)

    1. $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$
    2. the reaction of aluminum oxide, carbon, and chlorine gas at 900ºC to produce aluminum chloride and carbon monoxide

11. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)

    1. the reaction of water and carbon at 800ºC to produce hydrogen and carbon monoxide
    2. $Mn(s) + S_8(s) + CaO(s) \rightarrow CaS(s) + MnO(s)$
    3. the reaction of ethylene and oxygen at elevated temperature in the presence of a silver catalyst to produce ethylene oxide

    
    
    Ethylene oxide

    4. $ZnS(s) + H_2SO_4(aq) + O_2(g) \rightarrow ZnSO_4(aq) + S_8(s) + H_2O(l)$

12. Silver is tarnished by hydrogen sulfide, an atmospheric contaminant, to form a thin layer of dark silver sulfide ($Ag_2S$) along with hydrogen gas.

    1. Write a balanced chemical equation for this reaction.
    2. Which species has been oxidized and which has been reduced?
    3. Assuming 2.2 g of Ag has been converted to silver sulfide, construct a table showing the reaction in terms of the number of atoms in the reactants and products, the moles of reactants and products, the grams of reactants and products, and the

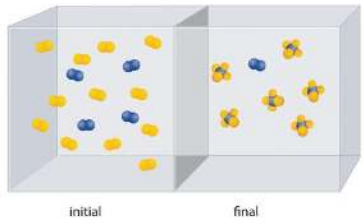
molecules of reactants and products.

13. The following reaction is used in the paper and pulp industry:

$Na_2SO_4(aq) + C(s) + NaOH(aq) \rightarrow Na_2CO_3(aq) + Na_2S(aq) + H_2O(l)$

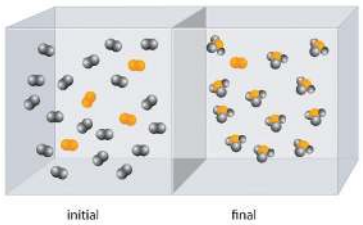
    1. Balance the chemical equation.
    2. Identify the oxidant and the reductant.
    3. How much carbon is needed to convert 2.8 kg of sodium sulfate to sodium sulfide?
    4. If the yield of the reaction were only 78%, how many kilograms of sodium carbonate would be produced from 2.80 kg of sodium sulfate?
    5. If 240 g of carbon and 2.80 kg of sodium sulfate were used in the reaction, what would be the limiting reactant (assuming an excess of sodium hydroxide)?

14. The reaction of $A_2$ (blue) with $B_2$ (yellow) is shown below. The initial reaction mixture is shown on the left and the mixture after the reaction has gone to completion is shown on the right.




    1. Write a balanced chemical equation for the reaction.
    2. Which is the limiting reactant in the initial reaction mixture?
    3. How many moles of the product $AB_4$ could you obtain from a mixture of 0.020 mol $A_2$ and 0.060 mol $B_2$?

15. The reaction of $X_4$ (orange) with $Y_2$ (black) is shown below. The initial reaction mixture is shown on the left and the mixture after the reaction has gone to completion is shown on the right.




    1. Write a balanced chemical equation for the reaction.
    2. Which is the limiting reactant in the initial reaction mixture?
    3. How many moles of the product $XY_3$ could you obtain from a mixture of 0.100 mol $X_4$ and 0.300 mol $Y_2$?

16. Methyl butyrate, an artificial apple flavor used in the food industry, is produced by the reaction of butanoic acid with methanol in the presence of an acid catalyst ($H^+$):

$$CH_3CH_2CH_2COOH\,(l) + CH_3OH\,(l) \overset{H^+}{\rightarrow} CH_3CH_2CH_2CO_2CH_3\,(l) + H_2O\,(l) \tag{3.5.7}$$

    1. Given 7.8 g of butanoic acid, how many grams of methyl butyrate would be synthesized, assuming 100% yield?
    2. The reaction produced 5.5 g of methyl butyrate. What was the percent yield?
    3. Is the catalyst used in this reaction heterogeneous or homogeneous?

17. In the presence of a platinum catalyst, hydrogen and bromine react at elevated temperatures (300°C) to form hydrogen bromide (heat is indicated by Δ):

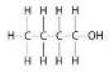
$$H_{2(g)} + Br_2\,(l) \overset{Pt}{\underset{\Delta}{\rightarrow}} 2HBr\,(g) \tag{3.5.8}$$

Given the following, calculate the mass of hydrogen bromide produced:

1. $8.23 \times 10^{22}$ molecules of $H_2$
2. $6.1 \times 10^{3}$ mol of $H_2$
3. $1.3 \times 10^{5}$ g of $H_2$
4. Is the catalyst used in this reaction heterogeneous or homogeneous?

## Answers

1. 1. redox reaction
   2. exchange
   3. acid–base
   4. condensation
2. 
3. 1. S, −2; N, −3; H, +1
   2. P, +5; O, −2
   3. F, −1; Al, +3
   4. S, −2; Cu, +2
   5. H, +1; O, −2; C, +4
   6. H, +1; N, −3
   7. H, +1; O, −2; S, +6
   8. H, +1, O, −2; C, +2
   9. butanol:

      O,−2; H, +1

      From left to right: C, −3–2–2–1
4. 
5. $2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$ acid–base reaction
6. 
7. 1. Ca, +2; O, −2; C, +4
   2. Na, +1; Cl, −1
   3. O, −2; C, +4
   4. K, +1; O, −2; Cr, +6
   5. K, +1; O, −2; Mn, +7
   6. O, −2; Fe, +3
   7. O, −2; H, +1; Cu, +2
   8. O, −2; S, +6
   9. Hexanol

      O,−2; H, +1

      From left to right: C: −3, −2, −2, −2, −2, −1
8. 
9. 1. Na is the reductant and is oxidized. $Cl_2$ is the oxidant and is reduced.
   2. Mg is the reductant and is oxidized. Si is the oxidant and is reduced.
   3. $H_2O_2$ is both the oxidant and reductant. One molecule is oxidized, and one molecule is reduced.
10. 

11. 1. $H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$

    C is the reductant and is oxidized. $H_2O$ is the oxidant and is reduced.

    2. $8Mn(s) + S_8(s) + 8CaO(s) \rightarrow 8CaS(s) + 8MnO(s)$

    Mn is the reductant and is oxidized. The $S_8$ is the oxidant and is reduced.

    3. $2C_2H_4(g) + O_2(g) \rightarrow 2C_2H_4O(g)$

    Ethylene is the reductant and is oxidized. $O_2$ is the oxidant and is reduced.

    4. $8ZnS(s) + 8H_2SO_4(aq) + 4O_2(g) \rightarrow 8ZnSO_4(aq) + S_8(s) + 8H_2O(l)$

    Sulfide in ZnS is the reductant and is oxidized. $O_2$ is the oxidant and is reduced.

12.

13. 1. $Na_2SO_4 + 2C + 4NaOH \rightarrow 2Na_2CO_3 + Na_2S + 2H_2O$
    2. The sulfate ion is the oxidant, and the reductant is carbon.
    3. 470 g
    4. 3300 g
    5. carbon

14.

15.

16.

17. 1. 22.1 g
    2. $9.9 \times 10^5$ g
    3. $1.0 \times 10^7$ g
    4. heterogeneous

## Contributors

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Modified by Joshua Halpern

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# 3.6: Chemical Reactions in the Atmosphere

**Learning Objectives**

- To become familiar with the various reactions implicated in the destruction of Earth's ozone layer.

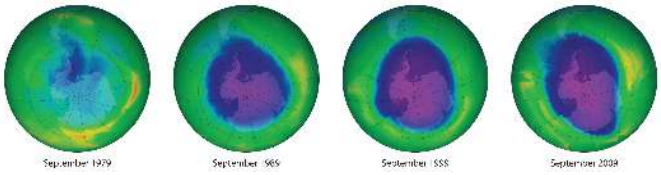
Section 3.5 "Types of Chemical Reactions" described different classes of chemical reactions. Of the many different chemical reactions that occur in Earth's atmosphere, some are important and controversial because they affect our quality of life and health. The atmospheric reactions presented in this section provide examples of the various classes of reactions introduced in this chapter that are implicated in the destruction of Earth's protective ozone layer.



Ozone, $O_3$

Each year since the mid-1970s, scientists have noted a disappearance of approximately 70% of the ozone (O3) layer above Antarctica during the Antarctic spring, creating what is commonly known as the "ozone hole." Ozone is an unstable form of oxygen that consists of three oxygen atoms bonded together. In September 2009, the Antarctic ozone hole reached 24.1 million km2 (9.3 million mi2), about the size of North America. The largest area ever recorded was in the year 2000, when the hole measured 29.9 million km2 and for the first time extended over a populated area—the city of Punta Arenas, Chile (population 154,000; Figure 3.6.1 ). A less extensive zone of depletion has been detected over the Arctic as well. Years of study from the ground, from the air, and from satellites in space have shown that chlorine from industrial chemicals used in spray cans, foam packaging, and refrigeration materials is largely responsible for the catalytic depletion of ozone through a series of condensation, cleavage, and oxidation–reduction reactions.

Figure 3.6.1 Satellite Photos of Earth Reveal the Sizes of the Antarctic Ozone Hole over Time



*Dark blue colors correspond to the thinnest ozone; light blue, green, yellow, orange, and red indicate progressively thicker ozone. In September 2000, the Antarctic ozone hole briefly approached a record 30 million $km^2$.*

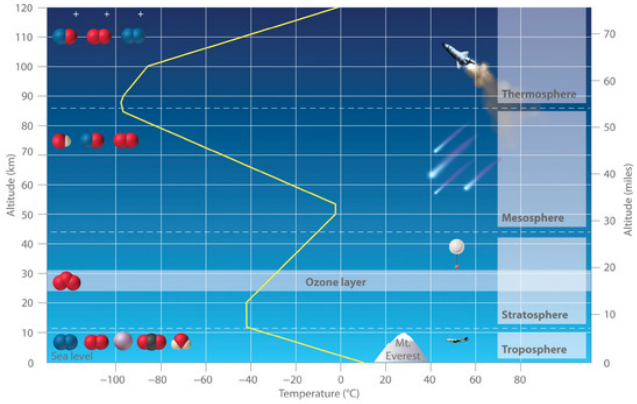
## Earth's Atmosphere and the Ozone Layer

Earth's atmosphere at sea level is an approximately 80:20 solution of nitrogen and oxygen gases, with small amounts of carbon dioxide, water vapor, and the noble gases, and trace amounts of a variety of other compounds (Table 3.2). A key feature of the atmosphere is that its composition, temperature, and pressure vary dramatically with altitude. Consequently, scientists have divided the atmosphere into distinct layers, which interact differently with the continuous flux of solar radiation from the top and the land and ocean masses at the bottom. Some of the characteristic features of the layers of the atmosphere are illustrated in Figure 3.6.2

Table 3.6.1 The Composition of Earth's Atmosphere at Sea Level*

| Gas | Formula | Volume (%) |
|---|---|---|
| nitrogen | $N_2$ | 78.084 |
| oxygen | $O_2$ | 20.948 |
| argon | Ar | 0.934 |
| carbon dioxide† | $CO_2$ | 0.0314 |
| neon | Ne | 0.00182 |
| helium | He | 0.000524 |
| krypton | Kr | 0.000114 |
| methane | $CH_4$ | 0.0002 |
| hydrogen | $H_2$ | 0.00005 |
| nitrous oxide | $N_2O$ | 0.00005 |
| xenon | Xe | 0.0000087 |
| * In addition, air contains as much as 7% water vapor (H2O), 0.0001% sulfur dioxide (SO2), 0.00007% ozone (O3), 0.000002% carbon monoxide (CO), and 0.000002% nitrogen dioxide (NO2). | | |
| † Carbon dioxide levels are highly variable; the typical range is 0.01–0.1%. | | |

Figure 3.6.2 Variation of Temperature with Altitude in Earth's Atmosphere




*Note the important chemical species present in each layer. The yellow line indicates the temperature at various altitudes.*

The troposphere is the lowest layer of the atmosphere, extending from Earth's surface to an altitude of about 11–13 km (7–8 mi). Above the troposphere lies the stratosphere, which extends from 13 km (8 mi) to about 44 km (27 mi). As shown in Figure 3.6.2, the temperature of the troposphere decreases steadily with increasing altitude. Because "hot air rises," this temperature gradient leads to continuous mixing of the upper and lower regions within the layer. The thermally induced turbulence in the troposphere produces fluctuations in temperature and precipitation that we collectively refer to as "weather." In contrast, mixing between the layers of the atmosphere occurs relatively slowly, so each layer has distinctive chemistry. We focus our attention on the stratosphere, which contains the highest concentration of ozone.

The sun's radiation is the major source of energy that initiates chemical reactions in the atmosphere. The sun emits many kinds of radiation, including visible light, which is radiation that the human eye can detect, and ultraviolet light, which is higher energy radiation that cannot be detected by the human eye. This higher energy ultraviolet light can cause a wide variety of chemical reactions that are harmful to organisms. For example, ultraviolet light is used to sterilize items, and, as anyone who has ever suffered a severe sunburn knows, it can produce extensive tissue damage.

Light in the higher energy ultraviolet range is almost totally absorbed by oxygen molecules in the upper layers of the atmosphere, causing the $O_2$ molecules to dissociate into two oxygen atoms in a cleavage reaction:

$$O_2(g) \overset{light}{\rightarrow} 2O(g) \tag{3.6.1}$$

Light is written above the arrow to indicate that light is required for the reaction to occur. The oxygen atoms produced in Equation 3.6.1 can undergo a condensation reaction with $O_2$ molecules to form ozone:

Extra close brace or missing open brace

Ozone is responsible for the pungent smell we associate with lightning discharges and electric motors. It is also toxic and a significant air pollutant, particularly in cities.

In the stratosphere, the ozone produced via Equation 3.6.3 has a major beneficial effect. Ozone absorbs the less-energetic range of ultraviolet light, undergoing a cleavage reaction in the process to give $O_2$ and O:

$$O_3(g) \overset{light}{\rightarrow} O_2(g) + O(g) \tag{3.6.2}$$

The formation of ozone (Equation 3.6.2 ) and its decomposition (Equation 3.6.3 ) are normally in balance, resulting in essentially constant levels of about $10^{15}$ ozone molecules per liter in the stratosphere. This so-called ozone layer acts as a protective screen that absorbs ultraviolet light that would otherwise reach Earth's surface.

In 1974, F. Sherwood Rowland and Mario Molina published a paper claiming that commonly used chlorofluorocarbon (CFC) compounds were causing major damage to the ozone layer (Table 3.3). CFCs had been used as refrigerants and propellants in aerosol cans for many years, releasing millions of tons of CFC molecules into the atmosphere. Because CFCs are volatile compounds that do not readily undergo chemical reactions, they persist in the atmosphere long enough to be carried to the top of the troposphere, where they eventually enter the stratosphere. There they are exposed to intense ultraviolet light and undergo a cleavage reaction to produce a chlorine atom, which is shown for Freon-11:

$$CCl_3F(g) \overset{light}{\rightarrow} CCl_2F(g) + Cl(g) \tag{3.6.3}$$

The resulting chlorine atoms act as a homogeneous catalyst in two redox reactions (Equation 3.6.5 and Equation 3.6.6 ):

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g) \tag{3.6.4}$$

Extra close brace or missing open brace

Adding the two reactions in Equation 3.6.5 and Equation 3.6.6 gives

$$Cl(g) + O_3(g) + ClO(g) + O(g) \rightarrow ClO(g) + Cl(g) + 2O_2(g) \tag{3.6.5}$$

Because chlorine and ClO (chlorine monoxide) appear on both sides of the equation, they can be canceled to give the following net reaction:

$$O_3(g) + O(g) \rightarrow 2O_2(g) \tag{3.6.6}$$

In the presence of chlorine atoms, one $O_3$ molecule and one oxygen atom react to give two $O_2$ molecules. Although chlorine is necessary for the overall reaction to occur, it does not appear in the net equation. The chlorine atoms are a catalyst that increases the rate at which ozone is converted to oxygen.

Table 3.6.2 Common CFCs and Related Compounds

| Name | Molecular Formula | Industrial Name |
|---|---|---|
| trichlorofluoromethane | $CCl_3F$ | CFC-11 (Freon-11) |
| dichlorodifluoromethane | $CCl_2F_2$ | CFC-12 (Freon-12) |
| chlorotrifluoromethane | $CClF_3$ | CFC-13 (Freon-13) |
| bromotrifluoromethane | $CBrF_3$ | Halon-1301* |
| bromochlorodifluoromethane | $CBrClF_2$ | Halon-1211 |

*Halons, compounds similar to CFCs that contain at least one bromine atom, are used as fire extinguishers in specific applications (e.g., the engine rooms of ships).

Because the stratosphere is relatively isolated from the layers of the atmosphere above and below it, once chlorine-containing species enter the stratosphere, they remain there for long periods of time. Each chlorine atom produced from a CFC molecule can lead to the destruction of large numbers of ozone molecules, thereby decreasing the concentration of ozone in the stratosphere. Eventually, however, the chlorine atom reacts with a water molecule to form hydrochloric acid, which is carried back into the troposphere and then washed out of the atmosphere in rainfall.

## The Ozone Hole

Massive ozone depletions were first observed in 1975 over the Antarctic and more recently over the Arctic. Although the reactions in Equation 3.6.4 and Equation 3.6.5 appear to account for most of the ozone destruction observed at low to middle latitudes, Equation 3.37 requires intense sunlight to generate chlorine atoms, and sunlight is in very short supply during the polar winters. At high latitudes (near the poles), therefore, a different set of reactions must be responsible for the depletion.

Recent research has shown that, in the absence of oxygen atoms, chlorine monoxide can react with stratospheric nitrogen dioxide in a redox reaction to form chlorine nitrate ($ClONO_2$). When chlorine nitrate is in the presence of trace amounts of HCl or adsorbed on ice particles in stratospheric clouds, additional redox reactions can occur in which chlorine nitrate produces $Cl_2$ or HOCl (hypochlorous acid):

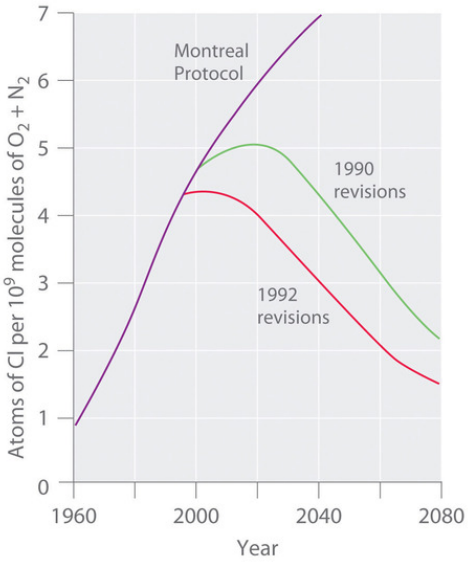
$$HCl(g) + ClONO_2(g) \rightarrow Cl_2(g) + HNO_3(g) \tag{3.6.7}$$

$$H_2O(g) + ClONO_2(g) \rightarrow HOCl(g) + HNO_3(g) \tag{3.6.8}$$

Both $Cl_2$ and HOCl undergo cleavage reactions by even weak sunlight to give reactive chlorine atoms. When the sun finally rises after the long polar night, relatively large amounts of $Cl_2$ and HOCl are present and rapidly generate high levels of chlorine atoms. The reactions shown in Equation 3.6.5 and Equation 3.6.6 then cause ozone levels to fall dramatically.

Stratospheric ozone levels decreased about 2.5% from 1978 to 1988, which coincided with a fivefold increase in the widespread use of CFCs since the 1950s. If the trend were allowed to continue, the results could be catastrophic. Fortunately, many countries have banned the use of CFCs in aerosols. In 1987, representatives from 43 nations signed the Montreal Protocol, committing themselves to reducing CFC emissions by 50% by the year 2000. Later, representatives from a large number of countries, alarmed by data showing the rapid depletion of stratospheric chlorine, agreed to phase out CFCs completely by the early 21st century; the United States banned their use in 1995. The projected effects of these agreements on atmospheric chlorine levels are shown in Figure 3.6.3. Because of the very slow rate at which CFCs are removed from the stratosphere, however, stratospheric chlorine levels will not fall to the level at which the Antarctic ozone hole was first observed until about 2050. The scientific community recognized Molina and Rowland's work in 1995, when they shared the Nobel Prize in Chemistry.

Figure 3.6.3Projected Effects of International Agreements on Atmospheric Chlorine Levels

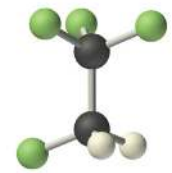



*The graph plots atmospheric chlorine content in chlorine atoms per 109 molecules of $O_2$ plus $N_2$from 1960 to 1990 (actual data) and 1990 to 2080 (estimated for various schemes for regulating CFC emissions).*

Manufacturing companies are now under great political and economic pressure to find alternatives to the CFCs used in the air-conditioning units of cars, houses, and commercial buildings. One approach is to use hydrochlorofluorocarbons (HCFCs), hydrocarbons in which only some of the hydrogen atoms are replaced by chlorine or fluorine, and hydrofluorocarbons (HFCs), which do not contain chlorine (Table 3.6.3 "Selected HCFCs and HFCs"). The C–H bonds in HCFCs and HFCs act as “handles” that permit additional chemical reactions to occur. Consequently, these substances are degraded more rapidly, and most are washed out of the atmosphere before they can reach the stratosphere.

Table 3.6.3 Selected HCFCs and HFCs

| Name | Molecular Formula | Industrial Name |
|---|---|---|
| chlorodifluoromethane | $CHClF_2$ | HCFC-22 (freon-22) |
| 1-chloro-1,1-difluoroethane | $CH_3CClF_2$ | HCFC-141b |
| 2,2-dichloro-1,1,1-trifluoroethane | $CHCl_2CF_3$ | HCFC-123 |
| 1,1,1,2-tetrafluoroethane | $CH_2FCF_3$ | HFC-134a |


HFC-134a, $CH_2FCF_3$

***HFCs are used as a replacement for CFCs**. The molecular structure of HFC-$_{134a}$ is shown in this ball-and-stick model.*

Nonetheless, the small fraction of HCFCs that reaches the stratosphere will deplete ozone levels just as CFCs do, so they are not the final answer. Indeed, the 1990 London amendment to the Montreal Protocol specifies that HCFCs must be phased out by 2040. Finding a suitable replacement for refrigerants is just one of the challenges facing chemists in the 21st century.

### Example 3.6.1

Nitric oxide (NO) may also be an important factor in the destruction of the ozone layer. One source of this compound is the combustion of hydrocarbons in jet engines. The fact that high-flying supersonic aircraft inject NO directly into the stratosphere was a major argument against the development of commercial supersonic transports. Do you agree with this decision? Why or why not?

**Given**: identity of compound

**Asked for**: assessment of likely role in ozone depletion

**Strategy**:

Predict what reactions are likely to occur between NO and ozone and then determine whether the reactions are likely to deplete ozone from the atmosphere.

**Solution**:

Both NO and $NO_2$ are known oxides of nitrogen. Thus NO is likely to react with ozone according to the chemical equation

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \tag{3.6.9}$$

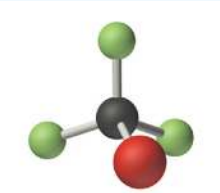
resulting in ozone depletion. If $NO_2$(g) also reacts with atomic oxygen according to the equation

$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g) \tag{3.6.10}$$

then we would have a potential catalytic cycle for ozone destruction similar to that caused by chlorine atoms. Based on these reactions, the development of commercial supersonic transports is not recommended until the environmental impact has undergone additional testing. (Although these reactions have been observed, they do not appear to be a major factor in ozone destruction.)

### Exercise 3.6.1

An industrial manufacturer proposed that halons such as $CF_3Br$ could be used as replacements for CFC propellants. Do you think that this is a reasonable suggestion or is there a potential problem with such a use?



Halon-1301, $CBrF_3$

**Answer**

The compound $CF_3Br$ contains carbon, fluorine, and a bromine atom that is chemically similar to chlorine. Studies have shown that bromine atoms are far more destructive of ozone than chlorine atoms. Halons are banned under the Montreal Protocols except for special uses where they cannot be replaced. This includes fire extinguishers on airplanes and to protect supercomputer systems.

## Summary

Earth's atmosphere consists of discrete layers that do not mix readily with one another. The sun emits radiation with a wide range of energies, including visible light, which can be detected by the human eye, and ultraviolet light, which is more energetic than visible light and cannot be detected by the human eye. In the stratosphere, ultraviolet light reacts with $O_2$ molecules to form atomic oxygen. Atomic oxygen then reacts with an $O_2$ molecule to produce ozone ($O_3$). As a result of this reaction, the stratosphere contains an appreciable concentration of ozone molecules that constitutes the ozone layer. The absorption of ultraviolet light in the

stratosphere protects Earth's surface from the sun's harmful effects. Volatile organic compounds that contain chlorine and fluorine, which are known as chlorofluorocarbons (CFCs), are capable of reaching the stratosphere, where they can react with ultraviolet light to generate chlorine atoms and other chlorine-containing species that catalyze the conversion of ozone to $O_2$, thereby decreasing the amount of $O_3$ in the stratosphere. Replacing chlorofluorocarbons with hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs) is one strategy that has been developed to minimize further damage to Earth's ozone layer.

## Key Takeaway

The composition of Earth's atmosphere is vulnerable to degradation through reactions with common industrial chemicals.

### Conceptual Problems

1. Carbon monoxide is a toxic gas that can be produced from the combustion of wood in wood-burning stoves when excess oxygen is not present. Write a balanced chemical equation showing how carbon monoxide is produced from carbon and suggest what might be done to prevent it from being a reaction product.
2. Explain why stratospheric ozone depletion has developed over the coldest part of Earth (the poles) and reaches a maximum at the beginning of the polar spring.
3. What type of reactions produce species that are believed to be responsible for catalytic depletion of ozone in the atmosphere?

### Numerical Problem

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7) before proceeding to the Numerical Problems.

1. Sulfur dioxide and hydrogen sulfide are important atmospheric contaminants that have resulted in the deterioration of ancient objects. Sulfur dioxide combines with water to produce sulfurous acid, which then reacts with atmospheric oxygen to produce sulfuric acid. Sulfuric acid is known to attack many metals that were used by ancient cultures. Give the formulas for these four sulfur-containing species. What is the percentage of sulfur in each compound? What is the percentage of oxygen in each?

## Contributors

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# 3.7: Essential Skills 2

**Topics**

- Proportions
- Percentages
- Unit Conversions

In Essential Skills 1 in Chapter 1 Section 1.8 , we introduced you to some of the fundamental mathematical operations you need to successfully manipulate mathematical equations in chemistry. Before proceeding to the problems in Chapter 7 you should become familiar with the additional skills described in this section on proportions, percentages, and unit conversions.

## Proportions

We can solve many problems in general chemistry by using ratios, or proportions. For example, if the ratio of some quantity $A$ to some quantity $B$ is known, and the relationship between these quantities is known to be constant, then any change in $A$ (from $A_1$ to $A_2$) produces a proportional change in $B$ (from $B_1$ to $B_2$) and vice versa. The relationship between $A_1$, $B_1$, $A_2$, and $B_2$ can be written as follows:

$$\frac{A_1}{B_1} = \frac{A_2}{B_2} = constant$$

To solve this equation for $A_2$, we multiply both sides of the equality by $B_2$, thus canceling $B_2$ from the denominator:

$$(B_2)\frac{A_1}{B_1} = \left(\cancel{B_2}\right)\frac{A_2}{\cancel{B_2}}$$

$$\frac{B_2 A_1}{B_1} = A_2$$

Similarly, we can solve for $B_2$ by multiplying both sides of the equality by $1/A_2$, thus canceling $A_2$ from the numerator:

$$\begin{aligned} \left(\frac{1}{A_2}\right)\frac{A_1}{A_1} &= \left(\frac{1}{\cancel{A_2}}\right)\frac{\cancel{A_2}}{B_2} \\ \frac{A_1}{A_2 B_1} &= \frac{1}{B_2} \end{aligned} \tag{3.7.1}$$

If the values of $A_1$, $A_2$, and $B_1$ are known, then we can solve the left side of the equation and invert the answer to obtain $B_2$:

$$B_2 = numerical\ value$$

$$B_2 = \frac{1}{numerical\ value}$$

If the value of $A_1$, $A_2$, or $B_1$ is unknown, however, we can solve for $B_2$ by inverting both sides of the equality:

$$B_2 = \frac{A_2 B_1}{A_1}$$

When you manipulate equations, remember that *any operation carried out on one side of the equality must be carried out on the other*.

Skill Builder ES1 illustrates how to find the value of an unknown by using proportions.

### Skill Builder ES1

If 38.4 g of element A are needed to combine with 17.8 g of element B, then how many grams of element A are needed to combine with 52.3 g of element B?

Solution

We set up the proportions as follows:

$$A_1 = 38.4\ g$$

$$B_1 = 17.8\ g$$

$$A_2 = ?$$

$$B_2 = 52.3\ g$$

$$\frac{A_1}{B_1} = \frac{A_2}{B_2}$$

$$\frac{38.4\ g}{17.8\ g} = \frac{A_2}{52.3\ g}$$

Multiplying both sides of the equation by 52.3 g gives

$$\frac{(38.4\ g)\,(52.3\ g)}{17.8\ g} = \frac{A_2\,(\cancel{52.3})}{\cancel{52.3}\ g}$$

$$A_2 = 113\ g$$

Notice that grams cancel to leave us with an answer that is in the correct units. *Always check to make sure that your answer has the correct units.*

### Skill Builder ES2

Solve to find the indicated variable.

1. $\frac{(16.4\ g)}{41.2\ g} = \frac{x}{18.3\ g}$
2. $\frac{(2.65\ m)}{4.02\ m} = \frac{3.28\ m}{y}$
3. $\frac{3.27\times10^{-3}\ g}{x} = \frac{5.0\times10^{-1}\ g}{3.2\ g}$
4. Solve for $V_1$: $\frac{P_1}{P_2} = \frac{V_2}{V_1}$
5. Solve for $T_1$: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Solution

1. Multiply both sides of the equality by 18.3 g to remove this measurement from the denominator: $(18.3\ g)\,\frac{16.4\ \cancel{g}}{41.2\ \cancel{g}} = \left(\cancel{18.3\ g}\right)\frac{x}{\cancel{18.3\ g}}$

$$7.28\ g = x$$

2, Multiply both sides of the equality by 1/3.28 m, solve the left side of the equation, and then invert to solve for *y*:

$$\left(\frac{1}{3.28\ m}\right)\frac{2.65\ m}{4.02\ m} = \left(\frac{1}{\cancel{3.28\ m}}\right)\frac{\cancel{3.28\ m}}{y} = \frac{1}{y}$$

$$y = \frac{(4.02)\,(3.28)}{2.65} = 4.98\ m$$

3. Multiply both sides of the equality by 1/3.27 × $10^{-3}$ g, solve the right side of the equation, and then invert to find *x*:

$$\left(\frac{1}{\cancel{3.27\times10^{-3}\ g}}\right)\frac{\cancel{3.27\times10^{-3}\ g}}{x} = \left(\frac{1}{3.27\times10^{-3}\ g}\right)\frac{5.0\times10^{-1}\ \cancel{g}}{3.2\ \cancel{g}} = \frac{1}{x}$$

$$x = \frac{(3.2\ g)\,(3.27\times10^{-3}\ g)}{5.0\times10^{-1}\ g} = 2.1\times10^{-2}\ g$$

1. Multiply both sides of the equality by $1/V_2$, and then invert both sides to obtain $V_1$: $\left(\frac{1}{V_2}\right)\frac{P_1}{P_2} = \left(\frac{1}{\cancel{V_2}}\right)\frac{\cancel{V_2}}{V_1}$

   $\frac{P_2V_2}{P_1} = V_1$
2. Multiply both sides of the equality by $1/P_1V_1$ and then invert both sides to obtain $T_1$: $\left(\frac{1}{\cancel{P_1V_1}}\right)\frac{\cancel{P_1V_1}}{T_1} = \left(\frac{1}{P_1V_1}\right)\frac{P_2V_2}{T_2}$

   $\frac{1}{T_1} = \frac{P_2V_2}{T_2P_1V_{1]}}$

   $T_1 = \frac{T_2P_1V_{1]}}{P_2V_2}$

## Percentages

Because many measurements are reported as percentages, many chemical calculations require an understanding of how to manipulate such values. You may, for example, need to calculate the mass percentage of a substance, as described in Section 11.2 , or determine the percentage of product obtained from a particular reaction mixture.

You can convert a percentage to decimal form by dividing the percentage by 100:

$$52.8\% = \frac{52.8}{100} = 0.528$$

Conversely, you can convert a decimal to a percentage by multiplying the decimal by 100:

$$0.356 \times 100 = 35.6\%$$

Suppose, for example, you want to determine the mass of substance *A*, one component of a sample with a mass of 27 mg, and you are told that the sample consists of 82% *A*. You begin by converting the percentage to decimal form:

$$82\% = \frac{82}{100} = 0.82$$

The mass of *A* can then be calculated from the mass of the sample:

$$0.82 \times 27\ mg = 22\ mg$$

Skill Builder ES3 provides practice in converting and using percentages.

### Skill Builder ES3

Convert each number to a percentage or a decimal.

1. 29.4%
2. 0.390
3. 101%
4. 1.023

Solution

1. $\frac{29.4}{100} = 0.294$
2. $0.390 \times \times 100 = 39.0$
3. $\frac{101}{100} = 1.01$
4. $1.023 \times 100 = 102.3\%$

### Skill Builder ES4

Use percentages to answer the following questions, being sure to use the correct number of significant figures (see Essential Skills 1 in Chapter 1 Section 1.8 ). Express your answer in scientific notation where appropriate.

1. What is the mass of hydrogen in 52.83 g of a compound that is 11.2% hydrogen?
2. What is the percentage of carbon in 28.4 g of a compound that contains 13.79 g of that element?
3. A compound that is 4.08% oxygen contains 194 mg of that element. What is the mass of the compound?

Solution

1. $52.83\ g \times \frac{11.2}{100} = 52.83\ g \times 0.112 = 5.92\ g$

2. $\frac{13.79\ g\ carbon}{28.4\ g} \times 100 = 48.6\%\ carbon$
3. This problem can be solved by using a proportion: $\frac{4.08\%\ oxygen}{100\%\ compound} \frac{194\ mg}{x\ mg}$

   $x = 4.75 \times 10^3\ mg\ \ (or\ 4.75\ g)$

## Unit Conversions

As you learned in Essential Skills 1 in Chapter 1, all measurements must be expressed in the correct units to have any meaning. This sometimes requires converting between different units (Table 1.8.1). Conversions are carried out using conversion factors, which are are ratios constructed from the relationships between different units or measurements. The relationship between milligrams and grams, for example, can be expressed as either 1 g/1000 mg or 1000 mg/1 g. When making unit conversions, use arithmetic steps accompanied by unit cancellation.

Suppose you have measured a mass in milligrams but need to report the measurement in kilograms. In problems that involve SI units, you can use the definitions of the prefixes given in Table 1.8.2 to get the necessary conversion factors. For example, you can convert milligrams to grams and then convert grams to kilograms:

$$milligrams \rightarrow grams \rightarrow kilograms\ 1000mg \rightarrow 1g\ 1000g \rightarrow 1\ kilogram$$

If you have measured 928 mg of a substance, you can convert that value to kilograms as follows:

$$928\ \cancel{mg} \times \frac{1\ g}{1000\ \cancel{mg}} = 0.928\ g$$

$$928\ \cancel{g} \times \frac{1\ kg}{1000\ \cancel{g}} = 0.000928\ kg = 9.28 \times 10^{-4}\ kg$$

In each arithmetic step, the units cancel as if they were algebraic variables, leaving us with an answer in kilograms. In the conversion to grams, we begin with milligrams in the numerator. Milligrams must therefore appear in the denominator of the conversion factor to produce an answer in grams. The individual steps may be connected as follows:

$$928\ \cancel{mg} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{1\ kg}{1000\ \cancel{g}} = \frac{928\ kg}{10^6} = 928 \times 10^{-6}\ kg = 9.28 \times 10^{-4}\ kg$$

Skill Builder ES5 provides practice converting between units.

### Skill Builder ES5

Use the information in Table 1.8.2 to convert each measurement. Be sure that your answers contain the correct number of significant figures and are expressed in scientific notation where appropriate.

1. 59.2 cm to decimeters
2. $3.7 \times 10^5$ mg to kilograms
3. 270 mL to cubic decimeters
4. $2.04 \times 10^3$ g to tons
5. $9.024 \times 10^{10}$ s to years

Solution

1. $59.2\ \cancel{cm} \times \frac{1\ \cancel{m}}{100\ \cancel{cm}} \times \frac{10\ dm}{1\ \cancel{m}} = 5.92\ dm$
2. $3.7 \times 10^5\ \cancel{mg} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{1\ kg}{1000\ \cancel{g}} = 3.7 \times 10^{-1}\ kg$
3. $270\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times \frac{1\ dm^3}{1\ \cancel{L}} = 270 \times 10^{-3}\ dm^3 = 2.70 \times 10^{-1}\ dm^3$
4. $2.04 \times 10^3\ \cancel{g} \times \frac{1\ \cancel{lb}}{453.6\ \cancel{g}} \times \frac{1\ tn}{2000\ \cancel{lb}} = 0.00225\ tn = 2.25 \times 10^{-3}\ tn$
5. $9.024 \times 10^{10}\ \cancel{s} \times \frac{1\ \cancel{min}}{60\ \cancel{s}} \times \frac{1\ \cancel{h}}{60\ \cancel{min}} \times \frac{1\ \cancel{d}}{24\ \cancel{h}} \times \frac{1\ yr}{365\ \cancel{d}} = 2.86 \times 10^3\ yr$

## Contributors

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Modified by Joshua Halpern

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# CHAPTER OVERVIEW

## 4: Reactions in Aqueous Solution


4.1: Aqueous Solutions
4.2: Solution Concentrations
4.3: Stoichiometry of Reactions in Solution
4.4: Ionic Equations
4.5: Precipitation Reactions
4.6: Acids and Bases
4.7: Acid Base Reactions
4.8: The Chemistry of Acid Rain
4.9: Quantitative Analysis Using Titration
4.10: Oxidation-Reduction Reactions
4.11: Essential Skills 3


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# 4.1: Aqueous Solutions

**Learning Objectives**

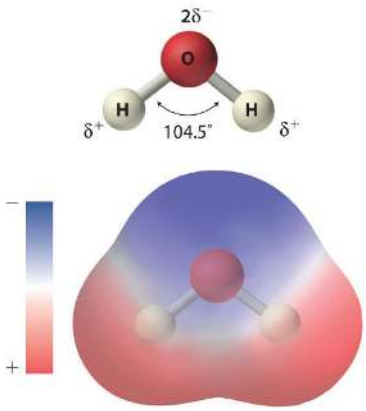
- To understand how and why solutions form.

The solvent in aqueous solutions is water, which makes up about 70% of the mass of the human body and is essential for life. Many of the chemical reactions that keep us alive depend on the interaction of water molecules with dissolved compounds. Moreover, the presence of large amounts of water on Earth's surface helps maintain its surface temperature in a range suitable for life. In this section, we describe some of the interactions of water with various substances and introduce you to the characteristics of aqueous solutions.

## Polar Substances

As shown in Figure 4.1.1, the individual water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. As is typical of group 16 elements, the oxygen atom in each O–H covalent bond attracts electrons more strongly than the hydrogen atom does. Consequently, the oxygen and hydrogen nuclei do not equally share electrons. Instead, hydrogen atoms are electron poor compared with a neutral hydrogen atom and have a partial positive charge, which is indicated by $\delta^+$. The oxygen atom, in contrast, is more electron rich than a neutral oxygen atom, so it has a partial negative charge. This charge must be twice as large as the partial positive charge on each hydrogen for the molecule to have a net charge of zero. Thus its charge is indicated by $2\delta^-$. This unequal distribution of charge creates a polar bond(Figure 4.1.1 ). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

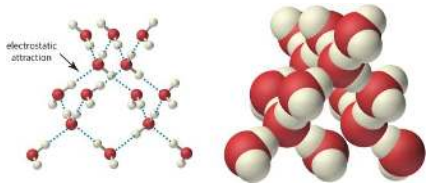
Figure 4.1.1 The Polar Nature of Water




*Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) and the hydrogen atoms are partially positively charged ($\delta^+$; red). For the molecule to have a net charge of zero, the partial negative charge on oxygen must be twice as large as the partial positive charge on each hydrogen.*

Because of the asymmetric charge distribution in the water molecule, adjacent water molecules are held together by attractive electrostatic ($\delta^+ \ldots \delta^-$) interactions between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms of adjacent molecules 4.1.2. Energy is needed to overcome these electrostatic attractions. In fact, without them, water would evaporate at a much lower temperature, and neither Earth's oceans nor we would exist!

Figure 4.1.2The Structure of Liquid Water




*Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms on adjacent molecules. As a result, the water molecules in liquid water form transient networks with structures similar to that shown. Because the interactions between water molecules are continually breaking and reforming, liquid water does not have a single fixed structure.*

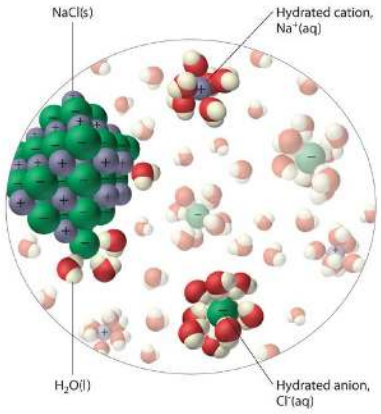
As you learned in Section 2.3, ionic compounds such as sodium chloride (NaCl) are also held together by electrostatic interactions—in this case, between oppositely charged ions in the highly ordered solid, where each ion is surrounded by ions of the opposite charge in a fixed arrangement. In contrast to an ionic solid, the structure of liquid water is not completely ordered because the interactions between molecules in a liquid are constantly breaking and reforming.

The unequal charge distribution in polar liquids such as water makes them good solvents for ionic compounds. When an ionic solid dissolves in water, the ions *dissociate*. That is, the partially negatively charged oxygen atoms of the $H_2O$ molecules surround the cations ($Na^+$ in the case of NaCl), and the partially positively charged hydrogen atoms in $H_2O$ surround the anions ($Cl^-$; Figure 4.1.3). Individual cations and anions that are each surrounded by their own shell of water molecules are called hydrated ions. We can describe the dissolution of NaCl in water as

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq)$$

where (aq) indicates that $Na^+$ and $Cl^-$ are hydrated ions.

Figure 4.1.3 The Dissolution of Sodium Chloride in Water




*An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations ($Na^+$) and the partially negatively charged oxygen atoms of water molecules, and between the anions ($Cl^-$) and the partially positively charged hydrogen atoms of water.*

### Note the Pattern

Polar liquids are good solvents for ionic compounds.

## Electrolytes

When electricity, in the form of an *electrical potential*, is applied to a solution, ions in solution migrate toward the oppositely charged rod or plate to complete an electrical circuit, whereas neutral molecules in solution do not (Figure 4.1.4). Thus solutions that contain ions conduct electricity, while solutions that contain only neutral molecules do not. Electrical current will flow through the circuit shown in Figure 4.1.4 and the bulb will glow *only* if ions are present. The lower the concentration of ions in solution, the

weaker the current and the dimmer the glow. Pure water, for example, contains only very low concentrations of ions, so it is a poor electrical conductor.

### Note the Pattern

Solutions that contain ions conduct electricity.

Figure 4.1.4 The Effect of Ions on the Electrical Conductivity of Water




*An electrical current will flow and light the bulb only if the solution contains ions. (a) Pure water or an aqueous solution of a nonelectrolyte allows almost no current to flow, and the bulb does not light. (b) A weak electrolyte produces a few ions, allowing some current to flow and the bulb to glow dimly. (c) A strong electrolyte produces many ions, allowing more current to flow and the bulb to shine brightly.*

An electrolyte is any compound that can form ions when it dissolves in water. When strong electrolytes dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure 4.1.4). Examples include ionic compounds such as barium chloride ($BaCl_2$) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

$$BaCl_2(s) \xrightarrow{H_2O(l)} Ba^{2+}(aq) + 2Cl^-(aq)$$

$$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

The single arrows from reactant to products in Equation 4.1.2 and Equation 4.1.3 indicate that dissociation is complete.

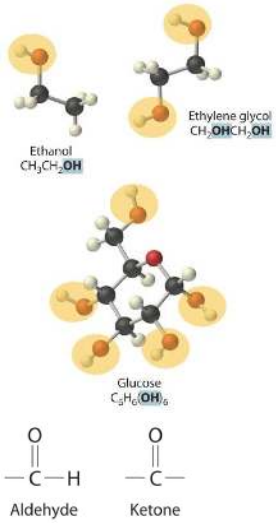
When weak electrolytes dissolve, they produce relatively few ions in solution. This does *not* mean that the compounds do not dissolve readily in water; many weak electrolytes contain polar bonds and are therefore very soluble in a polar solvent such as water. They do not completely dissociate to form ions, however, because of their weaker electrostatic interactions with the solvent. Because very few of the dissolved particles are ions, aqueous solutions of weak electrolytes do not conduct electricity as well as

solutions of strong electrolytes. One such compound is acetic acid ($CH_3CO_2H$), which contains the $–CO_2H$ unit. Although it is soluble in water, it is a weak acid and therefore also a weak electrolyte. Similarly, ammonia ($NH_3$) is a weak base and therefore a weak electrolyte. The behavior of weak acids and weak bases will be described in more detail when we discuss acid–base reactions in Section 8.6 .

Nonelectrolytes A substance that dissolves in water to form neutral molecules and has essentially no effect on electrical conductivity. that dissolve in water do so as neutral molecules and thus have essentially no effect on conductivity. Examples of nonelectrolytes that are very soluble in water but that are essentially nonconductive are ethanol, ethylene glycol, glucose, and sucrose, all of which contain the –OH group that is characteristic of alcohols. In Section 8.6, we will discuss why alcohols and carboxylic acids behave differently in aqueous solution; for now, however, you can simply look for the presence of the –OH and $–CO_2H$ groups when trying to predict whether a substance is a strong electrolyte, a weak electrolyte, or a nonelectrolyte. In addition to alcohols, two other classes of organic compounds that are nonelectrolytes are aldehydesA class of organic compounds that has the general form RCHO, in which the carbon atom of the carbonyl group is bonded to a hydrogen atom and an R group. The R group may be either another hydrogen atom or an alkyl group (c.f. ketone). and ketones). The alkyl groups may be the same or different., whose general structures are shown here. The distinctions between soluble and insoluble substances and between strong, weak, and nonelectrolytes are illustrated in Figure 4.1.5 .

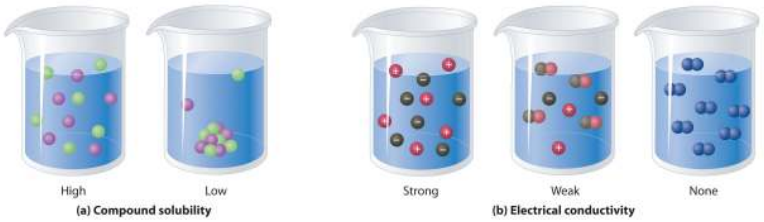
## Note the Pattern

Ionic substances and carboxylic acids are electrolytes; alcohols, aldehydes, and ketones are nonelectrolytes.




**General structure of an aldehyde and a ketone.** Notice that both contain the C=O group.

Figure 4.1.5 The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b)

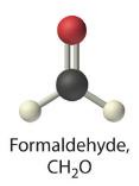



*When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated with one another in the solid. A soluble compound is a strong electrolyte if it dissociates completely into ions, a weak electrolyte if it dissociates only slightly into ions, and a nonelectrolyte if it dissolves to produce only neutral molecules.*

## Example 4.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

1. formaldehyde




2. cesium chloride

**Given:** compound

**Asked for:** relative ability to form ions in water

**Strategy:**

**A** Classify the compound as ionic or covalent.

**B** If the compound is ionic and dissolves, it is a strong electrolyte that will dissociate in water completely to produce a solution that conducts electricity well. If the compound is covalent and organic, determine whether it contains the carboxylic acid group. If the compound contains this group, it is a weak electrolyte. If not, it is a nonelectrolyte.

**Solution:**

1. **A** Formaldehyde is an organic compound, so it is covalent. **B** It contains an aldehyde group, not a carboxylic acid group, so it should be a nonelectrolyte.
2. **A** Cesium chloride (CsCl) is an ionic compound that consists of $Cs^+$ and $Cl^-$ ions. **B** Like virtually all other ionic compounds that are soluble in water, cesium chloride will dissociate completely into $Cs^+(aq)$ and $Cl^-(aq)$ ions. Hence it should be a strong electrolyte.

## Exercise 4.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

1. $CH_3)_2CHOH$ (2-propanol)




2. ammonium sulfate

**Answer**

1. nonelectrolyte
2. strong electrolyte

### Summary

Most chemical reactions are carried out in *solutions*, which are homogeneous mixtures of two or more substances. In a solution, a *solute* (the substance present in the lesser amount) is dispersed in a *solvent* (the substance present in the greater amount). *Aqueous solutions* contain water as the solvent, whereas *nonaqueous solutions* have solvents other than water.

Polar substances, such as water, contain asymmetric arrangements of **polar bonds**, in which electrons are shared unequally between bonded atoms. Polar substances and ionic compounds tend to be most soluble in water because they interact favorably with its structure. In aqueous solution, dissolved ions become **hydrated**; that is, a shell of water molecules surrounds them.

Substances that dissolve in water can be categorized according to whether the resulting aqueous solutions conduct electricity. **Strong electrolytes** dissociate completely into ions to produce solutions that conduct electricity well. **Weak electrolytes** produce a relatively small number of ions, resulting in solutions that conduct electricity poorly. **Nonelectrolytes** dissolve as uncharged molecules and have no effect on the electrical conductivity of water.

## Key Takeaway

- Aqueous solutions can be classified as polar or nonpolar depending on how well they conduct electricity.

## Conceptual Problems

1. What are the advantages to carrying out a reaction in solution rather than simply mixing the pure reactants?
2. What types of compounds dissolve in polar solvents?
3. Describe the charge distribution in liquid water. How does this distribution affect its physical properties?
4. Must a molecule have an asymmetric charge distribution to be polar? Explain your answer.
5. Why are many ionic substances soluble in water?
6. Explain the phrase *like dissolves like*.
7. What kinds of covalent compounds are soluble in water?
8. Why do most aromatic hydrocarbons have only limited solubility in water? Would you expect their solubility to be higher, lower, or the same in ethanol compared with water? Why?
9. Predict whether each compound will dissolve in water and explain why.
    a. toluene
    b. acetic acid
    c. sodium acetate
    d. butanol
    e. pentanoic acid
10. Predict whether each compound will dissolve in water and explain why.
    a. ammonium chloride
    b. 2-propanol
    c. heptane
    d. potassium dichromate
    e. 2-octanol
11. Given water and toluene, predict which is the better solvent for each compound and explain your reasoning.
    a. sodium cyanide
    b. benzene
    c. acetic acid
    d. sodium ethoxide ($CH_3CH_2ONa$)
12. Of water and toluene, predict which is the better solvent for each compound and explain your reasoning.
    a. *t*-butanol
    b. calcium chloride
    c. sucrose
    d. cyclohexene
13. Compound *A* is divided into three equal samples. The first sample does not dissolve in water, the second sample dissolves only slightly in ethanol, and the third sample dissolves completely in toluene. What does this suggest about the polarity of *A*?
14. You are given a mixture of three solid compounds—*A*, *B*, and *C*—and are told that *A* is a polar compound, *B* is slightly polar, and *C* is nonpolar. Suggest a method for separating these three compounds.

15. A laboratory technician is given a sample that contains only sodium chloride, sucrose, and cyclodecanone (a ketone). You must tell the technician how to separate these three compounds from the mixture. What would you suggest?
16. Many over-the-counter drugs are sold as ethanol/water solutions rather than as purely aqueous solutions. Give a plausible reason for this practice.
17. What distinguishes a weak electrolyte from a strong electrolyte?
18. Which organic groups result in aqueous solutions that conduct electricity?
19. It is considered highly dangerous to splash barefoot in puddles during a lightning storm. Why?
20. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.
    a. an aqueous solution of sodium chloride
    b. a solution of ethanol in water
    c. a solution of calcium chloride in water
    d. a solution of sucrose in water
21. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.
    a. an aqueous solution of acetic acid
    b. an aqueous solution of potassium hydroxide
    c. a solution of ethylene glycol in water
    d. a solution of ammonium chloride in water
22. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution? Explain your reasoning.
    a. potassium hydroxide
    b. ammonia
    c. calcium chloride
    d. butanoic acid
23. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution? Explain your reasoning.
    a. magnesium hydroxide
    b. butanol
    c. ammonium bromide
    d. pentanoic acid
24. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in aqueous solution? Explain your reasoning.
    a. $H_2SO_4$
    b. diethylamine
    c. 2-propanol
    d. ammonium chloride
    e. propanoic acid

## Answers

1.
2.
3.
4.
5. Ionic compounds such as NaCl are held together by electrostatic interactions between oppositely charged ions in the highly ordered solid. When an ionic compound dissolves in water, the partially negatively charged oxygen atoms of the $H_2O$ molecules surround the cations, and the partially positively charged hydrogen atoms in $H_2O$ surround the anions. The favorable

electrostatic interactions between water and the ions compensate for the loss of the electrostatic interactions between ions in the solid.

6.
7.
8.
9. a. Because toluene is an aromatic hydrocarbon that lacks polar groups, it is unlikely to form a homogenous solution in water.
   b. Acetic acid contains a carboxylic acid group attached to a small alkyl group (a methyl group). Consequently, the polar characteristics of the carboxylic acid group will be dominant, and acetic acid will form a homogenous solution with water.
   c. Because most sodium salts are soluble, sodium acetate should form a homogenous solution with water.
   d. Like all alcohols, butanol contains an −OH group that can interact well with water. The alkyl group is rather large, consisting of a 4-carbon chain. In this case, the nonpolar character of the alkyl group is likely to be as important as the polar character of the –OH, decreasing the likelihood that butanol will form a homogeneous solution with water.
   e. Like acetic acid, pentanoic acid is a carboxylic acid. Unlike acetic acid, however, the alkyl group is rather large, consisting of a 4-carbon chain as in butanol. As with butanol, the nonpolar character of the alkyl group is likely to be as important as the polar character of the carboxylic acid group, making it unlikely that pentanoic acid will form a homogeneous solution with water. (In fact, the solubility of both butanol and pentanoic acid in water is quite low, only about 3 g per 100 g water at 25°C.)
10.
11.
12.
13.
14.
15.
16.
17. An *electrolyte* is any compound that can form ions when it dissolves in water. When a strong electrolyte dissolves in water, it dissociates completely to give the constituent ions. In contrast, when a weak electrolyte dissolves in water, it produces relatively few ions in solution.
18.
19.
20.
21.
22.
23.
24.

## Contributors

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Modified by Joshua Halpern (Howard University)

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# 4.2: Solution Concentrations

**Learning Objectives**

- To describe the concentrations of solutions quantitatively

All of us have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the concentration. The quantity of solute that is dissolved in a particular quantity of solvent or solution. of a solution describes the quantity of a solute that is contained in a particular quantity of solvent or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for reactions that occur in solution. Chemists use many different ways to define concentrations, some of which are described in this section.

## Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is a common unit of concentration and is the number of moles of solute present in exactly $1L$ of solution $(mol/L)$ of a solution is the number of moles of solute present in exactly $1L$ of solution. Molarity is also the number of millimoles of solute present in exactly 1 mL of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution}$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as $M$. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the concentration of a solute. So

$$[\text{sucrose}] = 1.00\ \text{M}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles$$

Example 4.2.1 illustrates the use of Equation 4.2.2 and Equation 4.2.3.

**Example 4.2.1**

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

**Given:** identity of solute and volume and molarity of solution

**Asked for:** amount of solute in moles

**Strategy:**

Use either Equation 4.2.2 or Equation 4.2.3, depending on the units given in the problem.

**Solution**

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation 4.2.2 is more useful:

$$moles\ NaOH = V_L M_{mol/L} = (2.50\ \cancel{L})\left(\frac{0.100\ mol}{\cancel{L}}\right) = 0.250\ mol\ NaOH$$

**Exercise 4.2.1**

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

**Answer**

41.6 mmol

Concentrations are often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million* (*ppm*), which is grams of solute per $10^6$ g of solution, or in *parts per billion* (*ppb*), which is grams of solute per $10^9$ g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table 4.2.1.

Table 4.2.1 Common Units of Concentration

| Concentration | Units |
|---|---|
| m/m | g of solute/g of solution |
| m/v | g of solute/mL of solution |
| ppm | g of solute/$10^6$ g of solution |
| | µg/mL |
| ppb | g of solute/$10^9$ g of solution |
| | ng/mL |

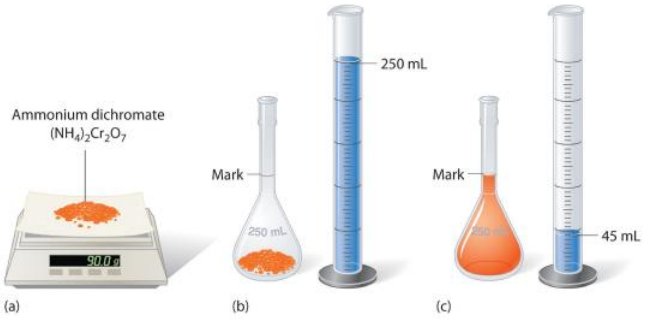
## The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 4.2.1 illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure 4.2.2, for some substances this effect can be significant, especially for concentrated solutions.

Figure 4.2.1 Preparation of a Solution of Known Concentration Using a Solid Solute




Figure 4.2.2 Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water




The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

### Example 4.2.2

The solution in Figure 4.2.1 contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2{\cdot}2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2{\cdot}2H_2O$?

**Given:** mass of solute and volume of solution

**Asked for:** concentration (M)

**Strategy:**

To find the number of moles of $CoCl_2{\cdot}2H_2O$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

**Solution**

The molar mass of $CoCl_2{\cdot}2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left( \frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol} \right) = 0.0603\ mol$$

The volume of the solution in liters is

$$volume = 500\ \cancel{mL} \left( \frac{1\ L}{1000\ \cancel{mL}} \right) = 0.500\ L$$

Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O$$

### Exercise 4.2.2

The solution shown in Figure 4.2.2 contains 90.0 g of $(NH_4)_2Cr_2O_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

**Answer**

$(NH_4)_2Cr_2O_7 = 1.43\ M$

To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 4.2.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 4.

### Example 4.2.3

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

**Given:** molarity, volume, and molar mass of solute

**Asked for:** mass of solute

**Strategy:**

**A** Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.

**B** Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

**Solution**

We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{mol/L} = moles$$

**A** $500\ \cancel{mL}\left(\dfrac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\dfrac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.155\ mol\ glucose$

**B** We then convert the number of moles of glucose to the required mass of glucose:

$$mass\ of\ glucose = 0.155\ \cancel{mol\ glucose}\left(\dfrac{180.16\ g\ glucose}{1\ \cancel{mol\ glucose}}\right) = 27.9\ g\ glucose$$

### Exercise 4.2.3

Another solution commonly used for intravenous injections is normal saline, a 0.16 M solution of sodium chloride in water. Calculate the mass of sodium chloride needed to prepare 250 mL of normal saline solution.

**Answer**

2.3 g NaCl

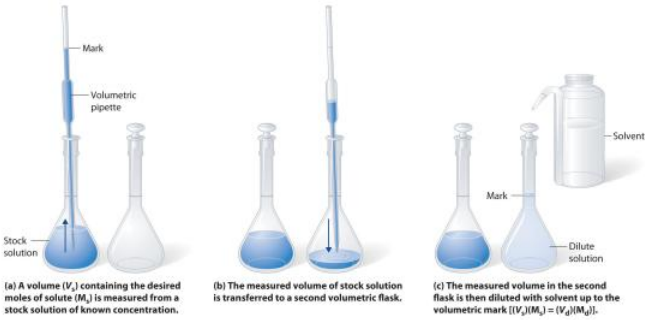
A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is a commercially prepared solution of known concentration, is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in Figure 4.2.3. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d)$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example 5 demonstrates the calculations involved in diluting a concentrated stock solution.

Figure 4.2.3 Preparation of a Solution of Known Concentration by Diluting a Stock Solution




*(a) A volume ($V_s$) containing the desired moles of solute ($M_s$) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].*

## Example 4.2.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4?

**Given:** volume and molarity of dilute solution

**Asked for:** volume of stock solution

**Strategy:**

**A** Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.

**B** To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

**Solution:**

**A** The D5W solution in Example 4 was 0.310 M glucose. We begin by using Equation 4.2.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$moles\ glucose = 2500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.775\ mol\ glucose$$

**B** We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$volume\ of\ stock\ soln = 0.775\ \cancel{mol\ glucose}\left(\frac{1\ L}{3.00\ \cancel{mol\ glucose}}\right) = 0.258\ L\ or\ 258\ mL$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.2.4 for $V_s$ and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500\ L)(0.310\ \cancel{M})}{3.00\ \cancel{M}} = 0.258\ L$$

As we have noted, there is often more than one correct way to solve a problem.

## Exercise 4.2.4

What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

**Answer**

16 mL

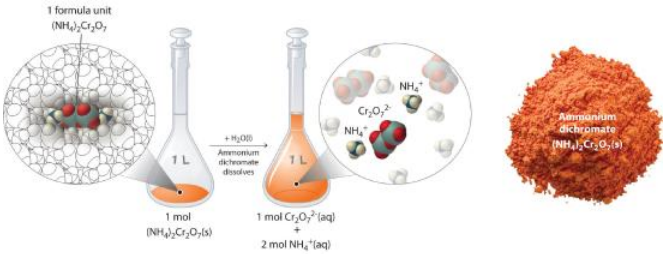
## Ion Concentrations in Solution

In Example 3, you calculated that the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL is 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two $NH_4^+$ ions and one $Cr_2O_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated $NH_4^+$ and $Cr_2O_7^{2-}$ ions:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq)$$

Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of $NH_4^+$ cations (see Figure 4.2.4 ).

Figure 4.2.4 Dissolution of 1 mol of an Ionic Compound




In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of $NH_4^+$ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

When we carry out a chemical reaction using a solution of a salt such as ammonium dichromate, we need to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(NH_4)_2Cr_2O_7$, then the concentration of $Cr_2O_7^{2-}$ must also be 1.43 M because there is one $Cr_2O_7^{2-}$ ion per formula unit. However, there are two $NH_4^+$ ions per formula unit, so the concentration of $NH_4^+$ ions is 2 × 1.43 M = 2.86 M. Because each formula unit of $(NH_4)_2Cr_2O_7$ produces *three* ions when dissolved in water ($2NH_4^+ + 1Cr_2O_7^{2-}$), the *total* concentration of ions in the solution is 3 × 1.43 M = 4.29 M.

## Example 4.2.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

1. 0.21 M NaOH
2. 3.7 M $(CH_3)CHOH$
3. 0.032 M $In(NO_3)_3$

**Given:** molarity

**Asked for:** concentrations

**Strategy:**

**A** Classify each compound as either a strong electrolyte or a nonelectrolyte.

**B** If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

**Solution:**

1. Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution:
$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$

   **B** Because each formula unit of NaOH produces one $Na^+$ ion and one $OH^-$ ion, the concentration of each ion is the same as the concentration of NaOH: $[Na^+]$ = 0.21 M and $[OH^-]$ = 0.21 M.

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –OH group, so it is an alcohol. Recall from Section 8.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

   **B** The only solute species in solution is therefore $(CH_3)_2CHOH$ molecules, so $[(CH_3)_2CHOH]$ = 3.7 M.

3. **A** Indium nitrate is an ionic compound that contains $In^{3+}$ ions and $NO_3^-$ ions, so we expect it to behave like a strong electrolyte in aqueous solution:

$$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

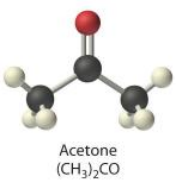
   **B** One formula unit of $In(NO_3)_3$ produces one $In^{3+}$ ion and three $NO_3^-$ ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M $In^{3+}$ and 3 × 0.032 M = 0.096 M $NO_3^-$—that is, $[In^{3+}]$ = 0.032 M and $[NO_3^-]$ = 0.096 M.

## Exercise 4.2.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

**Answer**

1. 0.0012 M $Ba(OH)_2$
2. 0.17 M $Na_2SO_4$
3. 0.50 M $(CH_3)_2CO$, commonly known as acetone




## Key Equations

**definition of molarity**

Equation 4.2.1 : $molarity = \dfrac{moles\ of\ solute}{liters\ of\ solution} = \dfrac{mmoles\ of\ solute}{milliliters\ of\ solution}$

**relationship among volume, molarity, and moles**

Equation 4.2.2 : $V_L M_{mol/L} = \cancel{L}\left(\dfrac{mol}{\cancel{L}}\right) = moles$

**relationship between volume and concentration of stock and dilute solutions**

Equation 4.2.4 : $(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d)$

## Summary

The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed as **molarity**, the number of moles of solute in 1 L of solution. Solutions of known concentration can be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

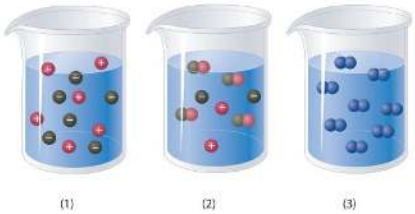
## Key Takeaway

- Solution concentrations are typically expressed as molarity and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

## Conceptual Problems

1. Which of the representations best corresponds to a 1 M aqueous solution of each compound? Justify your answers.

    a. $NH_3$
    b. HF
    c. $CH_3CH_2CH_2OH$
    d. $Na_2SO_4$




2. Which of the representations shown in Problem 1 best corresponds to a 1 M aqueous solution of each compound? Justify your answers.

    a. $CH_3CO_2H$
    b. NaCl
    c. $Na_2S$
    d. $Na_3PO_4$
    e. acetaldehyde

3. Would you expect a 1.0 M solution of $CaCl_2$ to be a better conductor of electricity than a 1.0 M solution of NaCl? Why or why not?

4. An alternative way to define the concentration of a solution is *molality*, abbreviated *m*. Molality is defined as the number of moles of solute in 1 kg of *solvent*. How is this different from molarity? Would you expect a 1 M solution of sucrose to be more or less concentrated than a 1 *m* solution of sucrose? Explain your answer.

5. What are the advantages of using solutions for quantitative calculations?

## Answer

1.
2.
3.
4.

5. If the amount of a substance required for a reaction is too small to be weighed accurately, the use of a solution of the substance, in which the solute is dispersed in a much larger mass of solvent, allows chemists to measure the quantity of the substance more accurately.

## Numerical Problems

1. Calculate the number of grams of solute in 1.000 L of each solution.

    a. 0.2593 M $NaBrO_3$
    b. 1.592 M $KNO_3$
    c. 1.559 M acetic acid
    d. 0.943 M potassium iodate

2. Calculate the number of grams of solute in 1.000 L of each solution.

a. 0.1065 M $BaI_2$
b. 1.135 M $Na_2SO_4$
c. 1.428 M $NH_4Br$
d. 0.889 M sodium acetate

3. If all solutions contain the same solute, which solution contains the greater mass of solute?

a. 1.40 L of a 0.334 M solution or 1.10 L of a 0.420 M solution
b. 25.0 mL of a 0.134 M solution or 10.0 mL of a 0.295 M solution
c. 250 mL of a 0.489 M solution or 150 mL of a 0.769 M solution

4. Complete the following table for 500 mL of solution.

| Compound | Mass (g) | Moles | Concentration (M) |
|---|---|---|---|
| calcium sulfate | 4.86 | | |
| acetic acid | | 3.62 | |
| hydrogen iodide dihydrate | | | 1.273 |
| barium bromide | 3.92 | | |
| glucose | | | 0.983 |
| sodium acetate | | 2.42 | |

5. What is the concentration of each species present in the following aqueous solutions?

a. 0.489 mol of $NiSO_4$ in 600 mL of solution
b. 1.045 mol of magnesium bromide in 500 mL of solution
c. 0.146 mol of glucose in 800 mL of solution
d. 0.479 mol of $CeCl_3$ in 700 mL of solution

6. What is the concentration of each species present in the following aqueous solutions?

a. 0.324 mol of $K_2MoO_4$ in 250 mL of solution
b. 0.528 mol of potassium formate in 300 mL of solution
c. 0.477 mol of $KClO_3$ in 900 mL of solution
d. 0.378 mol of potassium iodide in 750 mL of solution

7. What is the molar concentration of each solution?

a. 8.7 g of calcium bromide in 250 mL of solution
b. 9.8 g of lithium sulfate in 300 mL of solution
c. 12.4 g of sucrose ($C_{12}H_{22}O_{11}$) in 750 mL of solution
d. 14.2 g of iron(III) nitrate hexahydrate in 300 mL of solution

8. What is the molar concentration of each solution?

a. 12.8 g of sodium hydrogen sulfate in 400 mL of solution
b. 7.5 g of potassium hydrogen phosphate in 250 mL of solution
c. 11.4 g of barium chloride in 350 mL of solution
d. 4.3 g of tartaric acid ($C_4H_6O_6$) in 250 mL of solution

9. Give the concentration of each reactant in the following equations, assuming 20.0 g of each and a solution volume of 250 mL for each reactant.

a. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow$
b. $Ca(OH)_2(aq) + H_3PO_4(aq) \rightarrow$
c. $Al(NO_3)_3(aq) + H_2SO_4(aq) \rightarrow$

d. $Pb(NO_3)_2(aq) + CuSO_4(aq) \rightarrow$
e. $Al(CH_3CO_2)_3(aq) + NaOH(aq) \rightarrow$

10. An experiment required 200.0 mL of a 0.330 M solution of $Na_2CrO_4$. A stock solution of $Na_2CrO_4$ containing 20.0% solute by mass with a density of 1.19 g/cm$^3$ was used to prepare this solution. Describe how to prepare 200.0 mL of a 0.330 M solution of $Na_2CrO_4$ using the stock solution.
11. Calcium hypochlorite [$Ca(OCl)_2$] is an effective disinfectant for clothing and bedding. If a solution has a $Ca(OCl)_2$ concentration of 3.4 g per 100 mL of solution, what is the molarity of hypochlorite?
12. Phenol ($C_6H_5OH$) is often used as an antiseptic in mouthwashes and throat lozenges. If a mouthwash has a phenol concentration of 1.5 g per 100 mL of solution, what is the molarity of phenol?
13. If a tablet containing 100 mg of caffeine ($C_8H_{10}N_4O_2$) is dissolved in water to give 10.0 oz of solution, what is the molar concentration of caffeine in the solution?
14. A certain drug label carries instructions to add 10.0 mL of sterile water, stating that each milliliter of the resulting solution will contain 0.500 g of medication. If a patient has a prescribed dose of 900.0 mg, how many milliliters of the solution should be administered?

## Answers

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. 0.48 M $ClO^-$
12.
13. $1.74 \times 10^{-3}$ M caffeine
14.

## Contributors

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Modified by Joshua Halpern (Howard University)

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# 4.3: Stoichiometry of Reactions in Solution

**Learning Objectives**

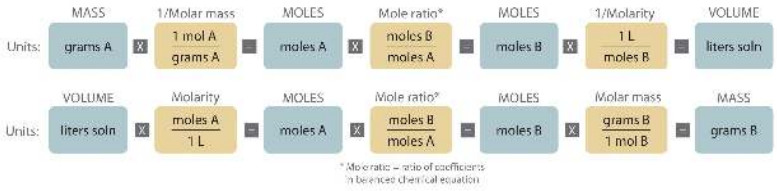
- To balance equations that describe reactions in solution.
- To solve quantitative problems involving the stoichiometry of reactions in solution.

Quantitative calculations involving reactions in solution are carried out in the same manner as we discussed in Chapter 3. Instead of *masses*, however, we use *volumes* of solutions of known concentration to determine the number of moles of reactants. Whether we are dealing with volumes of solutions of reactants or masses of reactants, the coefficients in the balanced chemical equation tell us the number of moles of each reactant needed and the number of moles of each product that can be produced.

## Calculating Moles from Volume

An expanded version of the flowchart for stoichiometric calculations illustrated in Figure 7.4.1 is shown in Figure 4.3.1. We can use the balanced chemical equation for the reaction and *either* the masses of solid reactants and products *or* the volumes of solutions of reactants and products to determine the amounts of other species, as illustrated in Example 7, Example 8, and Example 9.

Figure 4.3.1 An Expanded Flowchart for Stoichiometric Calculations




*Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.*

### Note the Pattern

The balanced chemical equation for a reaction and either the masses of solid reactants and products or the volumes of solutions of reactants and products can be used in stoichiometric calculations.

**Example 4.3.1**

Gold is extracted from its ores by treatment with an aqueous cyanide solution, which causes a reaction that forms the soluble $[Au(CN)_2]^-$ ion. Gold is then recovered by reduction with metallic zinc according to the following equation:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

What mass of gold would you expect to recover from 400.0 L of a $3.30 \times 10^{-4}$ M solution of $[Au(CN)_2]^-$?

**Given:** chemical equation and molarity and volume of reactant

**Asked for:** mass of product

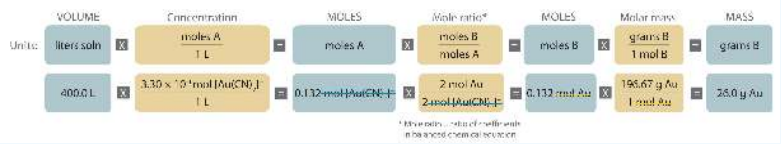
**Strategy:**

**A** Check the chemical equation to make sure it is balanced as written; balance if necessary. Then calculate the number of moles of $[Au(CN)_2]^-$ present by multiplying the volume of the solution by its concentration.

**B** From the balanced chemical equation, use a mole ratio to calculate the number of moles of gold that can be obtained from the reaction. To calculate the mass of gold recovered, multiply the number of moles of gold by its molar mass.

**Solution**

The equation is balanced as written, so we can proceed to the stoichiometric calculation. We can adapt Figure 8.3.1 for this particular problem as follows:




As indicated in the strategy, we start by calculating the number of moles of $[Au(CN)_2]^-$ present in the solution from the volume and concentration of the $[Au(CN)_2]^-$ solution:

$$\begin{aligned} moles\ [Au(CN)_2]^- &= V_L M_{mol/L} \\ &= 400.0\ \cancel{L}\left(\frac{3.30\times10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \end{aligned}$$

**B** Because the coefficients of gold and the $[Au(CN)_2]^-$ ion are the same in the balanced chemical equation, if we assume that Zn(s) is present in excess, the number of moles of gold produced is the same as the number of moles of $[Au(CN)_2]^-$ we started with (i.e., 0.132 mol of Au). The problem asks for the mass of gold that can be obtained, so we need to convert the number of moles of gold to the corresponding mass using the molar mass of gold:

$$\begin{aligned} mass\ of\ Au &= (moles\ Au)(molar\ mass\ Au) \\ &= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \end{aligned}$$

At a 2011 market price of over $1400 per troy ounce (31.10 g), this amount of gold is worth $1170.

$$26.0\ \cancel{g\ Au} \times \frac{1\ \cancel{troy\ oz}}{31.10\ \cancel{g}} \times \frac{\$1400}{1\ \cancel{troy\ oz\ Au}} = \$1170$$

Add text here.

## Exercise 4.3.1

What mass of solid lanthanum(III) oxalate nonahydrate $[La_2(C_2O_4)_3{\cdot}9H_2O]$ can be obtained from 650 mL of a 0.0170 M aqueous solution of $LaCl_3$ by adding a stoichiometric amount of sodium oxalate?

**Answer**

3.89 g

## Limiting Reactants in Solutions

The concept of limiting reactants applies to reactions that are carried out in solution as well as to reactions that involve pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 4.3.2.

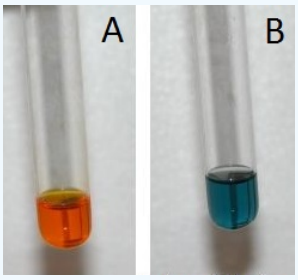
## Example 4.3.2

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3CH_3CH_2OH(aq) + \underset{yellow-orange}{2Cr_2O_7^{2-}}(aq) + 16H^+(aq) \xrightarrow[H_2SO_4(aq)]{Ag^+} 3CH_3CO_2H(aq) + \underset{green}{4Cr^{3+}}(aq) + 11H_2O(l)$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $Cr_2O_7^{2-}$ ions are reduced from $Cr^{6+}$ to $Cr^{3+}$. In the presence of $Ag^+$ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $Cr_2O_7^{2-}$ ion (the reactant) is yellow-orange and the $Cr^{3+}$ ion (the

product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.




**A Breathalyzer ampul before (a) and after (b) ethanol is added.** When a measured volume of a suspect's breath is bubbled through the solution, the ethanol is oxidized to acetic acid, and the solution changes color from yellow-orange to green. The intensity of the green color indicates the amount of ethanol in the sample.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% $H_2SO_4$ as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the $Cr^{6+}$ to $Cr^{3+}$?

**Given:** volume and concentration of one reactant

**Asked for:** mass of other reactant needed for complete reaction

**Strategy:**

**A** Calculate the number of moles of $Cr_2O_7^{2-}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.

**B** Find the total number of moles of $Cr_2O_7^{2-}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).

**C** Use the mole ratios from the balanced chemical equation to calculate the number of moles of $C_2H_5OH$ needed to react completely with the number of moles of $Cr_2O_7^{2-}$ ions present. Then find the mass of $C_2H_5OH$ needed by multiplying the number of moles of $C_2H_5OH$ by its molar mass.

**Solution**

**A** In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which we can use to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5 \times 10^{-7}\ moles$$

**B** Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $Cr_2O_7^{2-}$ when it dissolves, each milliliter of solution contains $8.5 \times 10^{-7}$ mol of $Cr_2O_7^{2-}$. The total number of moles of $Cr_2O_7^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5 \times 10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6 \times 10^{-6}\ mol\ Cr_2O_7^{2-}$$

**C** The balanced chemical equation tells us that 3 mol of $C_2H_5OH$ is needed to consume 2 mol of $Cr_2O_7^{2-}$ ion, so the total number of moles of $C_2H_5OH$ required for complete reaction is

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol\ Cr_2O_7^{2-}})\left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol\ Cr_2O_7^{2-}}}\right) = 3.9 \times 10^{-6}\ mol\ C_2H_5OH$$

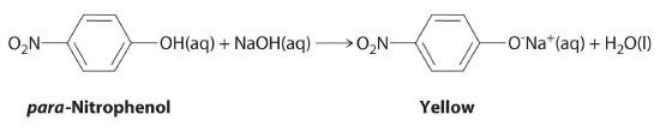
As indicated in the strategy, this number can be converted to the mass of $C_2H_5OH$ using its molar mass:

$$mass\ C_2H_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ C_2H_5OH}) \left(\frac{46.07\ g}{\cancel{mol\ C_2H_5OH}}\right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

Thus $1.8 \times 10^{-4}$ g or 0.18 mg of $C_2H_5OH$ must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

## Exercise 4.3.2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction




Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing $7.20 \times 10^{-4}$ g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

**Answer**

$4.93 \times 10^{-5}$ L or 49.3 µL

In Example 4.3.3 and Example 4.3.4, the identity of the limiting reactant has been apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, we can determine which reactant is limiting by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation, just as we did in Section 3.4 . The only difference is that now we use the volumes and concentrations of solutions of reactants rather than the masses of reactants to calculate the number of moles of reactants, as illustrated in Example 9.

## Example 4.3.3

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq)$$

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $K_2Cr_2O_7$ are mixed with 250 mL of 0.57 M $AgNO_3$?

**Given:** balanced chemical equation and volume and concentration of each reactant

**Asked for:** mass of product

**Strategy:**

**A** Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.

**B** Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.

**C** Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

**Solution**

**A** The balanced chemical equation tells us that 2 mol of $AgNO_3$(aq) reacts with 1 mol of $K_2Cr_2O_7$(aq) to form 1 mol of $Ag_2Cr_2O_7$(s) (Figure 8.3.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL} \left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right) \left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

**B** Now we can determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$K_2Cr_2O_7:\ \frac{0.085\ mol}{1\ mol} = 0.085$$

$$AgNO_3:\ \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $AgNO_3$ is the limiting reactant.

**C** Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only 0.14/2 = 0.070 mol of $Ag_2Cr_2O_7$. Finally, we convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The $Ag^+$ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the $K^+$ and $NO_3^-$ ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

## ? Exercise 4.3.3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2CO_2(g) + Na_2SO_4(aq) + 2H_2O(l)$$

If 13.0 mL of 3.0 M $H_2SO_4$ are added to 732 mL of 0.112 M $NaHCO_3$, what mass of $CO_2$ is produced?

**Answer**

3.4 g

## Summary

Quantitative calculations that involve the stoichiometry of reactions in solution use volumes of solutions of known concentration instead of masses of reactants or products. The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

## Key Takeaway

- Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation.

## Conceptual Problems

1. What information is required to determine the mass of solute in a solution if you know the molar concentration of the solution?
2. Is it possible for one reactant to be limiting in a reaction that does not go to completion?

## Numerical Problems

1. Refer to the Breathalyzer test described in Example 8. How much ethanol must be present in 89.5 mL of a person's breath to consume all the potassium dichromate in a Breathalyzer ampul containing 3.0 mL of a 0.40 mg/mL solution of potassium dichromate?
2. Phosphoric acid and magnesium hydroxide react to produce magnesium phosphate and water. If 45.00 mL of 1.50 M phosphoric acid are used in the reaction, how many grams of magnesium hydroxide are needed for the reaction to go to completion?
3. Barium chloride and sodium sulfate react to produce sodium chloride and barium sulfate. If 50.00 mL of 2.55 M barium chloride are used in the reaction, how many grams of sodium sulfate are needed for the reaction to go to completion?

4. How many grams of sodium phosphate are obtained in solution from the reaction of 75.00 mL of 2.80 M sodium carbonate with a stoichiometric amount of phosphoric acid? A second product is water; what is the third product? How many grams of the third product are obtained?
5. How many grams of ammonium bromide are produced from the reaction of 50.00 mL of 2.08 M iron(II) bromide with a stoichiometric amount of ammonium sulfide? What is the second product? How many grams of the second product are produced?
6. Lead(II) nitrate and hydroiodic acid react to produce lead(II) iodide and nitric acid. If 3.25 g of lead(II) iodide were obtained by adding excess HI to 150.0 mL of lead(II) nitrate, what was the molarity of the lead(II) nitrate solution?
7. Silver nitrate and sodium chloride react to produce sodium nitrate and silver chloride. If 2.60 g of AgCl was obtained by adding excess NaCl to 100 mL of $AgNO_3$, what was the molarity of the silver nitrate solution?

## Contributors

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# 4.4: Ionic Equations

**Learning Objectives**

- To understand what information is obtained by each type of ionic equation

The chemical equations discussed in Chapter 3 showed the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

Let's consider the reaction of silver nitrate with potassium dichromate. As you learned in Example 4.3.3, when aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equation

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq) \tag{4.4.1}$$

Although Equation ??? gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as $AgNO_3$ and $K_2Cr_2O_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $Ag_2Cr_2O_7$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation, showing which ions and molecules are hydrated and which are present in other forms and phases:

$$\begin{aligned} &2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \\ &\rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq) \end{aligned} \tag{4.4.2}$$

Note that $K^+$(aq) and $NO_3^-$(aq) ions are present on both sides of the equation, and their coefficients are the same on both sides. These ions are called spectator ions because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation, which shows only those species that participate in the chemical reaction:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{4.4.3}$$

Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In Equation 4.4.2, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $Ag_2Cr_2O_7$ formula unit.

By eliminating the spectator ions, we can focus on the chemistry that takes place in a solution. For example, the overall chemical equation for the reaction between silver fluoride and ammonium dichromate is as follows:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{4.4.4}$$

The complete ionic equation for this reaction is as follows:

$$\begin{aligned} &2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \\ &\rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq) \end{aligned} \tag{4.4.5}$$

Because two $NH_4^+$(aq) and two $F^-$(aq) ions appear on both sides of Equation ???, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 4.4.6 ), which is identical to Equation 4.4.5 :

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{4.4.6}$$

If we look at net ionic equations, it becomes apparent that many different combinations of reactants can result in the same net chemical reaction. For example, we can predict that silver fluoride could be replaced by silver nitrate in the preceding reaction without affecting the outcome of the reaction.

## Example 4.4.1

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium phosphate to give solid barium phosphate and a solution of sodium nitrate.

**Given:** reactants and products

**Asked for:** overall, complete ionic, and net ionic equations

**Strategy:**

Write and balance the overall chemical equation. Write all the soluble reactants and products in their dissociated form to give the complete ionic equation; then cancel species that appear on both sides of the complete ionic equation to give the net ionic equation.

**Solution**

From the information given, we can write the unbalanced chemical equation for the reaction:

$$Ba(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq)$$

Because the product is $Ba_3(PO_4)_2$, which contains three $Ba^{2+}$ ions and two $PO_4^{3-}$ ions per formula unit, we can balance the equation by inspection:

$$3Ba(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq)$$

This is the overall balanced chemical equation for the reaction, showing the reactants and products in their undissociated form. To obtain the complete ionic equation, we write each soluble reactant and product in dissociated form:

$$3Ba^{2+}(aq) + 6NO_3^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) + 6Na^+(aq) + 6NO_3^-(aq)$$

The six $NO_3^-$(aq) ions and the six $Na^+$(aq) ions that appear on both sides of the equation are spectator ions that can be canceled to give the net ionic equation:

$$3Ba^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s)$$

## Exercise 4.4.1

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous silver fluoride with aqueous sodium phosphate to give solid silver phosphate and a solution of sodium fluoride.

**Answer**

overall chemical equation:

$$3AgF(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaF(aq)$$

complete ionic equation:

$$3Ag^+(aq) + 3F^-(aq) + 3Na^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) + 3Na^+(aq) + 3F^-(aq)$$

net ionic equation:

$$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$$

So far, we have always indicated whether a reaction will occur when solutions are mixed and, if so, what products will form. As you advance in chemistry, however, you will need to predict the results of mixing solutions of compounds, anticipate what kind of reaction (if any) will occur, and predict the identities of the products. Students tend to think that this means they are supposed to "just know" what will happen when two substances are mixed. Nothing could be further from the truth: an infinite number of chemical reactions is possible, and neither you nor anyone else could possibly memorize them all. Instead, you must begin by identifying the various reactions that *could* occur and then assessing which is the most probable (or least improbable) outcome.

The most important step in analyzing an unknown reaction is to *write down all the species—whether molecules or dissociated ions—that are actually present in the solution* (not forgetting the solvent itself) so that you can assess which species are most likely to react with one another. The easiest way to make that kind of prediction is to attempt to place the reaction into one of several familiar classifications, refinements of the five general kinds of reactions introduced in Chapter 3 (acid–base, exchange, condensation, cleavage, and oxidation–reduction reactions). In the sections that follow, we discuss three of the most important kinds of reactions that occur in aqueous solutions: precipitation reactions (also known as exchange reactions), acid–base reactions, and oxidation–reduction reactions.

## Summary

The chemical equation for a reaction in solution can be written in three ways. The **overall chemical equation** shows all the substances present in their undissociated forms; the **complete ionic equation** shows all the substances present in the form in which they actually exist in solution; and the **net ionic equation** is derived from the complete ionic equation by omitting all **spectator ions**, ions that occur on both sides of the equation with the same coefficients. Net ionic equations demonstrate that many different combinations of reactants can give the same net chemical reaction.

## Key Takeaway

- A complete ionic equation consists of the net ionic equation and spectator ions.

## Conceptual Problem

1. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

## Contributors

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# 4.5: Precipitation Reactions

**Learning Objectives**

- To identify a precipitation reaction and predict solubilities

A precipitation reactionA subclass of an exchange reaction that yields an insoluble product (a precipitate) when two solutions are mixed. is a reaction that yields an insoluble product—a precipitateThe insoluble product that forms in a precipitation reaction.—when two solutions are mixed. In Section 3.4, we described a precipitation reaction in which a colorless solution of silver nitrate was mixed with a yellow-orange solution of potassium dichromate to give a reddish precipitate of silver dichromate:

$$AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq) \tag{4.5.1}$$

This equation has the general form of an exchange reaction:

$$AC + BD \rightarrow \underset{insoluble}{AD} + BC \tag{4.5.2}$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called *double-displacement reactions*. Two important uses of precipitation reactions are to isolate metals that have been extracted from their ores and to recover precious metals for recycling.

### Note the Pattern

Precipitation reactions are a subclass of exchange reactions.

## Predicting Solubilities

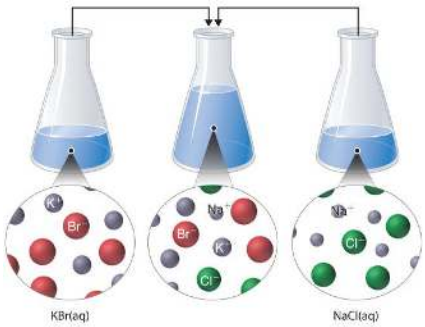
Table 4.5.1 gives guidelines for predicting the solubility of a wide variety of ionic compounds. To determine whether a precipitation reaction will occur, we identify each species in the solution and then refer to Table 4.5.1 to see which, if any, combination(s) of cation and anion are likely to produce an insoluble salt. In doing so, it is important to recognize that *soluble* and *insoluble* are relative terms that span a wide range of actual solubilities. We will discuss solubilities in more detail in the second semester, where you will learn that very small amounts of the constituent ions remain in solution even after precipitation of an "insoluble" salt. For our purposes, however, we will assume that precipitation of an insoluble salt is complete.

Table 4.5.1 Guidelines for Predicting the Solubility of Ionic Compounds in Water

| | **Soluble** | | **Exceptions** |
|---|---|---|---|
| Rule 1 | most salts that contain an alkali metal ($Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) and ammonium ($NH_4^+$) | | |
| Rule 2 | most salts that contain the nitrate ($NO_3^-$) anion | | |
| Rule 3 | most salts of anions derived from monocarboxylic acids (e.g., $CH_3CO_2^-$) | but not | silver acetate and salts of long-chain carboxylates |
| Rule 4 | most chloride, bromide, and iodide salts | but not | salts of metal ions located on the lower right side of the periodic table (e.g., $Cu^+$, $Ag^+$, $Pb^{2+}$, and $Hg_2^{2+}$). |
| | **Insoluble** | | **Exceptions** |
| Rule 5 | most salts that contain the hydroxide ($OH^-$) and sulfide ($S^{2-}$) anions | but not | salts of the alkali metals (group 1), the heavier alkaline earths ($Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ in group 2), and the $NH_4^+$ ion. |
| Rule 6 | most carbonate ($CO_3^{2-}$) and phosphate ($PO_4^{3-}$) salts | but not | salts of the alkali metals or the $NH_4^+$ ion. |
| Rule 7 | most sulfate ($SO_4^{2-}$) salts that contain main group cations with a charge ≥ +2 | but not | salts of +1 cations, $Mg^{2+}$, and dipositive transition metal cations (e.g., $Ni^{2+}$) |

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of a 1.0 M aqueous NaCl solution is mixed with 500 mL of a 1.0 M aqueous KBr solution, the final solution has a volume of 1.00 L and contains 0.50 M $Na^+(aq)$, 0.50 M $Cl^-(aq)$, 0.50 M $K^+(aq)$, and 0.50 M $Br^-(aq)$. As you will see in the following sections, none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other (Figure 4.5.1 ).

Figure 4.5.1 The Effect of Mixing Aqueous KBr and NaCl Solutions




*Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)*

## Example 4.5.1

Using the information in Table 4.5.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

1. Aqueous solutions of barium chloride and lithium sulfate are mixed.
2. Aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.
3. Aqueous solutions of strontium bromide and aluminum nitrate are mixed.
4. Solid lead(II) acetate is added to an aqueous solution of ammonium iodide.

**Given:** reactants

**Asked for:** reaction and net ionic equation

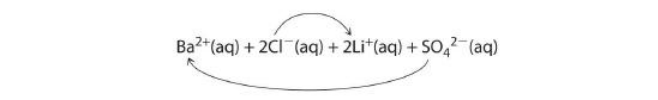
**Strategy:**

**A** Identify the ions present in solution and write the products of each possible exchange reaction.

**B** Refer to Table 4.5.1 to determine which, if any, of the products is insoluble and will therefore form a precipitate. If a precipitate forms, write the net ionic equation for the reaction.

**Solution**

1. **A** Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains $Ba^{2+}$, $Cl^-$, $Li^+$, and $SO_4^{2-}$ ions. The only possible exchange reaction is to form LiCl and $BaSO_4$:



http://chemwiki.ucdavis.edu/Wikitext...tion_Reactions

**B** We now need to decide whether either of these products is insoluble. Table 8.2 shows that LiCl is soluble in water (rules 1 and 4), but $BaSO_4$ is not soluble in water (rule 5). Thus $BaSO_4$ will precipitate according to the net ionic equation

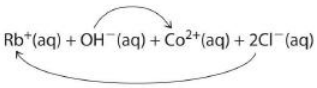
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Although soluble barium salts are toxic, $BaSO_4$ is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a “barium milkshake” or a “barium enema”—a suspension of very fine $BaSO_4$ particles in water.



**An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.”** A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. From Wikipedia

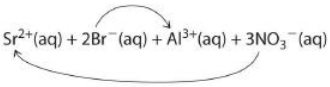
2. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains $Rb^+$, $OH^-$, $Co^{2+}$, and $Cl^-$ ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):




**B** According to Table 4.5.1, RbCl is soluble (rules 1 and 4), but $Co(OH)_2$ is not soluble (rule 5). Hence $Co(OH)_2$ will precipitate according to the following net ionic equation:

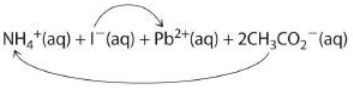
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

3. **A** When aqueous solutions of strontium bromide and aluminum nitrate are mixed, we initially obtain a solution that contains $Sr^{2+}$, $Br^-$, $Al^{3+}$, and $NO_3^-$ ions. The two possible products from an exchange reaction are aluminum bromide and strontium nitrate:




**B** According to Table 4.5.1 both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

4. **A** According to Table 4.5.1, lead acetate is soluble (rule 3). Thus solid lead acetate dissolves in water to give $Pb^{2+}$ and $CH_3CO_2^-$ ions. Because the solution also contains $NH_4^+$ and $I^-$ ions, the possible products of an exchange reaction are ammonium acetate and lead(II) iodide:




**B** According to Table 8.2, ammonium acetate is soluble (rules 1 and 3), but $PbI_2$ is insoluble (rule 4). Thus $Pb(C_2H_3O_2)_2$ will dissolve, and $PbI_2$ will precipitate. The net ionic equation is as follows:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

## ? Exercise 4.5.1

Using the information in Table 4.5.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

1. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
2. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
3. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
4. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

**Answer**

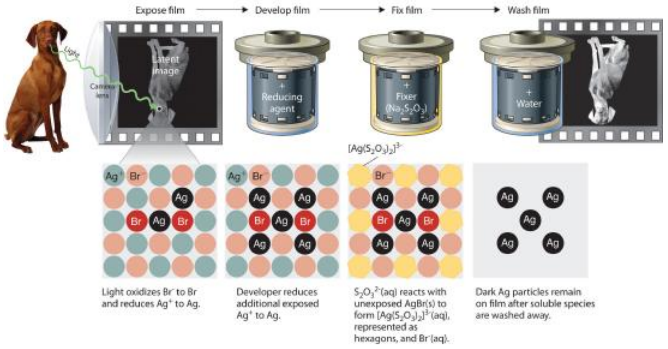
1. $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
2. $2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$
3. $NaF(s)$ dissolves; no net reaction
4. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

## Precipitation Reactions in Photography

Precipitation reactions can be used to recover silver from solutions used to develop conventional photographic film. Although largely supplanted by digital photography, conventional methods are often used for artistic purposes. Silver bromide is an off-white solid that turns black when exposed to light, which is due to the formation of small particles of silver metal. Black-and-white photography uses this reaction to capture images in shades of gray, with the darkest areas of the film corresponding to the areas that received the most light. The first step in film processing is to enhance the black/white contrast by using a developer to increase the amount of black. The developer is a reductant: because silver atoms catalyze the reduction reaction, grains of silver bromide that have already been partially reduced by exposure to light react with the reductant much more rapidly than unexposed grains.

After the film is developed, any unexposed silver bromide must be removed by a process called “fixing”; otherwise, the entire film would turn black with additional exposure to light. Although silver bromide is insoluble in water, it is soluble in a dilute solution of sodium thiosulfate ($Na_2S_2O_3$; *photographer’s hypo*) because of the formation of $[Ag(S_2O_3)_2]^{3-}$ ions. Thus washing the film with thiosulfate solution dissolves unexposed silver bromide and leaves a pattern of metallic silver granules that constitutes the negative. This procedure is summarized in Figure 4.5.2. The negative image is then projected onto paper coated with silver halides, and the developing and fixing processes are repeated to give a positive image. (Color photography works in much the same way, with a combination of silver halides and organic dyes superimposed in layers.) “Instant photo” operations can generate more than a hundred gallons of dilute silver waste solution per day. Recovery of silver from thiosulfate fixing solutions involves first removing the thiosulfate by oxidation and then precipitating $Ag^+$ ions with excess chloride ions.

Figure 4.5.2 Outline of the Steps Involved in Producing a Black-and-White Photograph




## Example 4.5.2

A silver recovery unit can process 1500 L of photographic silver waste solution per day. Adding excess solid sodium chloride to a 500 mL sample of the waste (after removing the thiosulfate as described previously) gives a white precipitate that, after filtration and drying, consists of 3.73 g of AgCl. What mass of NaCl must be added to the 1500 L of silver waste to ensure that all the $Ag^+$ ions precipitate?

**Given:** volume of solution of one reactant and mass of product from a sample of reactant solution

**Asked for:** mass of second reactant needed for complete reaction

**Strategy:**

**A** Write the net ionic equation for the reaction. Calculate the number of moles of AgCl obtained from the 500 mL sample and then determine the concentration of $Ag^+$ in the sample by dividing the number of moles of AgCl formed by the volume of solution.

**B** Determine the total number of moles of $Ag^+$ in the 1500 L solution by multiplying the $Ag^+$ concentration by the total volume.

**C** Use mole ratios to calculate the number of moles of chloride needed to react with $Ag^+$. Obtain the mass of NaCl by multiplying the number of moles of NaCl needed by its molar mass.

**Solution**

We can use the data provided to determine the concentration of $Ag^+$ ions in the waste, from which the number of moles of $Ag^+$ in the entire waste solution can be calculated. From the net ionic equation, we can determine how many moles of $Cl^-$ are needed, which in turn will give us the mass of NaCl necessary.

**A** The first step is to write the net ionic equation for the reaction:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

We know that 500 mL of solution produced 3.73 g of AgCl. We can convert this value to the number of moles of AgCl as follows:

$$moles\ AgCl = \frac{grams\ AgCl}{molar\ mass\ AgCl} = 3.73\ \cancel{g\ AgCl}\left(\frac{1\ mol\ AgCl}{143.32\ \cancel{g\ AgCl}}\right) = 0.0260\ mol\ AgCl$$

Therefore, the 500 mL sample of the solution contained 0.0260 mol of $Ag^+$. The $Ag^+$ concentration is determined as follows:

$$[Ag^+] = \frac{moles\ Ag^+}{liters\ soln} = \frac{0.0260\ mol\ AgCl}{0.500\ L} = 0.0520\ M$$

**B** The total number of moles of $Ag^+$ present in 1500 L of solution is as follows:

$$moles\ Ag^+ = 1500\ \cancel{L}\left(\frac{0.520\ mol}{1\ \cancel{L}}\right) = 78.1\ mol\ Ag^+$$

**C** According to the net ionic equation, one $Cl^-$ ion is required for each $Ag^+$ ion. Thus 78.1 mol of NaCl are needed to precipitate the silver. The corresponding mass of NaCl is

$$mass\ NaCl = 78.1\ \cancel{mol\ NaCl}\left(\frac{58.44\ g\ NaCl}{1\ \cancel{mol\ NaCl}}\right) = 4560\ g\ NaCl = 4.56\ kg\ NaCl$$

Note that 78.1 mol of AgCl correspond to 8.43 kg of metallic silver, which is worth about $7983 at 2011 prices ($32.84 per troy ounce). Silver recovery may be economically attractive as well as ecologically sound, although the procedure outlined is becoming nearly obsolete for all but artistic purposes with the growth of digital photography.

### ? Exercise 4.5.2

Because of its toxicity, arsenic is the active ingredient in many pesticides. The arsenic content of a pesticide can be measured by oxidizing arsenic compounds to the arsenate ion ($AsO_4^{3-}$), which forms an insoluble silver salt ($Ag_3AsO_4$). Suppose you are asked to assess the purity of technical grade sodium arsenite ($NaAsO_2$), the active ingredient in a pesticide used against termites. You dissolve a 10.00 g sample in water, oxidize it to arsenate, and dilute it with water to a final volume of 500 mL. You then add excess $AgNO_3$ solution to a 50.0 mL sample of the arsenate solution. The resulting precipitate of $Ag_3AsO_4$ has a mass of 3.24 g after drying. What is the percentage by mass of $NaAsO_2$ in the original sample?

**Answer**

91.0%

## Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when solutions of two substances are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

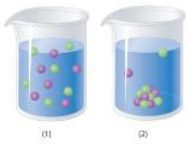
## Key Takeaway

- Predicting the solubility of ionic compounds in water can give insight into whether or not a reaction will occur.

## Conceptual Problems

1. Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.
   a. $FeCl_2(aq) + Na_2S(aq)$
   b. $NaOH(aq) + H_3PO_4(aq)$
   c. $ZnCl_2(aq) + (NH_4)_2S(aq)$
2. Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.
   a. $KOH(aq) + H_3PO_4(aq)$
   b. $K_2CO_3(aq) + BaCl_2(aq)$
   c. $Ba(NO_3)_2(aq) + Na_2SO_4(aq)$
3. Which representation best corresponds to an aqueous solution originally containing each of the following?
   a. 1 M $NH_4Cl$

b. 1 M $NaO_2CCH_3$
c. 1 M NaOH + 1 M HCl
d. 1 M $Ba(OH)_2$ + 1 M $H_2SO_4$



4. Which representation in Problem 3 best corresponds to an aqueous solution originally containing each of the following?

a. 1 M $CH_3CO_2H$ + 1 M NaOH
b. 1 M $NH_3$ + 1 M HCl
c. 1 M $Na_2CO_3$ + 1 M $H_2SO_4$
d. 1 M $CaCl_2$ + 1 M $H_3PO_4$

## Answer

1.
2.
3. a. 1
   b. 1
   c. 1
   d. 2
4.

## Numerical Problems

1. What mass of precipitate would you expect to obtain by mixing 250 mL of a solution containing 4.88 g of $Na_2CrO_4$ with 200 mL of a solution containing 3.84 g of $AgNO_3$? What is the final nitrate ion concentration?
2. Adding 10.0 mL of a dilute solution of zinc nitrate to 246 mL of 2.00 M sodium sulfide produced 0.279 g of a precipitate. How many grams of zinc(II) nitrate and sodium sulfide were consumed to produce this quantity of product? What was the concentration of each ion in the original solutions? What is the concentration of the sulfide ion in solution after the precipitation reaction, assuming no further reaction?

## Answer

1. 3.75 g $Ag_2CrO_4$; $5.02 \times 10^{-2}$ M nitrate
2.

## Contributors

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Modified by Joshua Halpern (Howard University)

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# 4.6: Acids and Bases

**Learning Objectives**

- To identify and name some common acids and bases

For our purposes at this point in the text, we can define an acidA substance with at least one hydrogen atom that can dissociate to form an anion and an $H^+$ ion (a proton) in aqueous solution, thereby foming an acidic solution. as a substance with at least one hydrogen atom that can dissociate to form an anion and an $H^+$ ion (a proton) in aqueous solution, thereby forming an *acidic solution*. We can define basesA substance that produces one or more hydroxide ions $OH^-$ and a cation when dissolved in aqueous solution, thereby forming a basic solution. as compounds that produce hydroxide ions ($OH^-$) and a cation when dissolved in water, thus forming a *basic solution*. Solutions that are neither basic nor acidic are *neutral*. This chapter discusses the nomenclature of common acids and identify some important bases. Pure acids and bases and their concentrated aqueous solutions are commonly encountered in the laboratory. They are usually highly corrosive, so they must be handled with care.

## Acids

The names of acids differentiate between (1) acids in which the $H^+$ ion is attached to an oxygen atom of a polyatomic anion (these are called oxoacidsAn acid in which the dissociable $H^+$ ion is attached to an oxygen atom of a polyatomic anion., or occasionally **oxyacids**) and (2) acids in which the $H^+$ ion is attached to some other element. In the latter case, the name of the acid begins with *hydro-* and ends in *-ic*, with the root of the name of the other element or ion in between. Recall that the name of the anion derived from this kind of acid always ends in *-ide*. Thus hydrogen chloride (HCl) gas dissolves in water to form hydrochloric acid (which contains $H^+$ and $Cl^-$ ions), hydrogen cyanide (HCN) gas forms hydrocyanic acid (which contains $H^+$ and $CN^-$ ions), and so forth (Table 4.6.1 ). Examples of this kind of acid are commonly encountered and very important. For instance, your stomach contains a dilute solution of hydrochloric acid to help digest food. When the mechanisms that prevent the stomach from digesting itself malfunction, the acid destroys the lining of the stomach and an ulcer forms.

### Note the Pattern

Acids are distinguished by whether the $H^+$ ion is attached to an oxygen atom of a polyatomic anion or some other element.

Table 4.6.1 Some Common Acids That Do Not Contain Oxygen

| Formula | Name in Aqueous Solution | Name of Gaseous Species |
|---|---|---|
| HF | hydrofluoric acid | hydrogen fluoride |
| HCl | hydrochloric acid | hydrogen chloride |
| HBr | hydrobromic acid | hydrogen bromide |
| HI | hydroiodic acid | hydrogen iodide |
| HCN | hydrocyanic acid | hydrogen cyanide |
| $H_2S$ | hydrosulfuric acid | hydrogen sulfide |

If an acid contains one or more $H^+$ ions attached to oxygen, it is a derivative of one of the common oxoanions, such as sulfate ($SO_4^{2-}$) or nitrate ($NO_3^-$). These acids contain as many $H^+$ ions as are necessary to balance the negative charge on the anion, resulting in a neutral species such as $H_2SO_4$ and $HNO_3$.

The names of acids are derived from the names of anions according to the following rules:

1. **If the name of the anion ends in *-ate*, then the name of the acid ends in *-ic*.** For example, because $NO_3^-$ is the nitrate ion, $HNO_3$ is nitric acid. Similarly, $ClO_4^-$ is the perchlorate ion, so $HClO_4$ is perchloric acid. Two important acids are sulfuric acid ($H_2SO_4$) from the sulfate ion ($SO_4^{2-}$) and phosphoric acid ($H_3PO_4$) from the phosphate ion ($PO_4^{3-}$). These two names use a slight variant of the root of the anion name: *sulf*ate becomes *sulfur*ic and *phosph*ate becomes *phosphor*ic.

2. **If the name of the anion ends in *-ite*, then the name of the acid ends in *-ous*.** For example, $OCl^-$ is the hypochlorite ion, and HOCl is hypochlorous acid; $NO_2^-$ is the nitrite ion, and $HNO_2$ is nitrous acid; and $SO_3^{2-}$ is the sulfite ion, and $H_2SO_3$ is sulfurous acid. The same roots are used whether the acid name ends in *-ic* or *-ous*; thus, *sulfite* becomes *sulfurous*.

The relationship between the names of the oxoacids and the parent oxoanions is illustrated in Figure 4.6.1, and some common oxoacids are in Table 4.6.2.

Figure 4.6.1 The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions

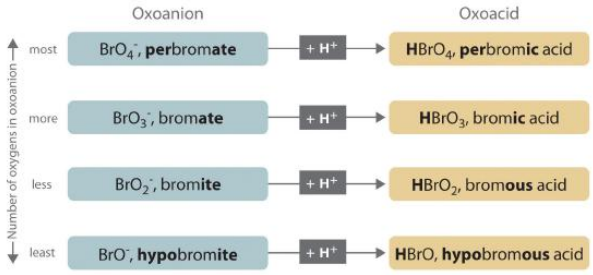



Table 4.6.2 Some Common Oxoacids

| Formula | Name |
|---|---|
| $HNO_2$ | nitrous acid |
| $HNO_3$ | nitric acid |
| $H_2SO_3$ | sulfurous acid |
| $H_2SO_4$ | sulfuric acid |
| $H_3PO_4$ | phosphoric acid |
| $H_2CO_3$ | carbonic acid |
| HClO | hypochlorous acid |
| $HClO_2$ | chlorous acid |
| $HClO_3$ | chloric acid |
| $HClO_4$ | perchloric acid |

**Example 4.6.1**

Name and give the formula for each acid.

1. the acid formed by adding a proton to the hypobromite ion ($OBr^-$)
2. the acid formed by adding two protons to the selenate ion ($SeO_4^{2-}$)

**Given:** anion

**Asked for:** parent acid

**Strategy:**

Refer to Table 4.6.1 and Table 4.6.2 to find the name of the acid. If the acid is not listed, use the guidelines given previously.

**Solution**

Neither species is listed in Table 4.6.1 or Table 4.6.2 so we must use the information given previously to derive the name of the acid from the name of the polyatomic anion.

1. The anion name, *hypobromite*, ends in *-ite*, so the name of the parent acid ends in *-ous*. The acid is therefore hypobromous acid (HOBr).
2. *Selenate* ends in *-ate*, so the name of the parent acid ends in *-ic*. The acid is therefore selenic acid ($H_2SeO_4$).

**? Exercise 4.6.1**

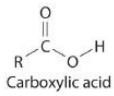
Name and give the formula for each acid.

1. the acid formed by adding a proton to the perbromate ion ($BrO_4^-$)
2. the acid formed by adding three protons to the arsenite ion ($AsO_3^{3-}$)

**Answer**

perbromic acid; $HBrO_4$ arsenous acid; $H_3AsO_3$

Many organic compounds contain the carbonyl groupA carbon atom double-bonded to an oxygen atom. It is a characteristic feature of many organic compounds, including carboxylic acids., in which there is a carbon–oxygen double bond. In carboxylic acidsAn organic compound that contains an −OH group covalently bonded to the carbon atom of a carbonyl group. The general formula of a carboxylic acid is $RCO_2H$. In water a carboxylic acid dissociates to produce an acidic solution., an –OH group is covalently bonded to the carbon atom of the carbonyl group. Their general formula is $RCO_2H$, sometimes written as RCOOH:



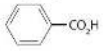
Carboxylic acid

where R can be an alkyl group, an aryl group, or a hydrogen atom. The simplest example, $HCO_2H$, is *formic acid*, so called because it is found in the secretions of stinging ants (from the Latin *formica*, meaning “ant”). Another example is *acetic acid* ($CH_3CO_2H$), which is found in vinegar. Like many acids, carboxylic acids tend to have sharp odors. For example, butyric acid ($CH_3CH_2CH_2CO_2H$), is responsible for the smell of rancid butter, and the characteristic odor of sour milk and vomit is due to lactic acid [$CH_3CH(OH)CO_2H$]. Some common


Lactic acid, $CH_3CH(OH)CO_2H$

carboxylic acids are shown in Figure 4.6.3.

Figure 4.6.3 Some Common Carboxylic Acids

| Formula (Structure) | Name | Uses |
|---|---|---|
| $HCO_2H$ | formic acid | tanning, dyeing |
| $CH_3CO_2H$ | acetic acid | vinegar, food preservative |
| $CH_3CH_2CO_2H$ | propionic acid | food preservative |
| $CH_3CH_2CH_2CO_2H$ | butyric acid | varnishes |
| $C_6H_5CO_2H$  | benzoic acid | food preservative, dyeing |

Although carboxylic acids are covalent compounds, when they dissolve in water, they dissociate to produce $H^+$ ions (just like any other acid) and $RCO_2^-$ ions. Note that *only the hydrogen attached to the oxygen atom of the $CO_2$ group dissociates to form an $H^+$ ion*. In contrast, the hydrogen atom attached to the oxygen atom of an alcohol does *not* dissociate to form an $H^+$ ion when an alcohol is dissolved in water.

### Note the Pattern

Only the hydrogen attached to the oxygen atom of the $CO_2$ group dissociates to form an $H^+$ ion.

## Bases

We will present more comprehensive definitions of bases in later chapters, but virtually every base you encounter in the meantime will be an ionic compound, such as sodium hydroxide (NaOH) and barium hydroxide [$Ba(OH)_2$], that contain the hydroxide ion and a metal cation. These have the general formula $M(OH)_n$. It is important to recognize that alcohols, with the general formula ROH, are covalent compounds, not ionic compounds; consequently, they do *not* dissociate in water to form a basic solution (containing $OH^-$ ions). When a base reacts with any of the acids we have discussed, it accepts a proton ($H^+$). For example, the hydroxide ion ($OH^-$) accepts a proton to form $H_2O$. Thus bases are also referred to as *proton acceptors*.



Methylamine

Concentrated aqueous solutions of ammonia ($NH_3$) contain significant amounts of the hydroxide ion, even though the dissolved substance is *not* primarily ammonium hydroxide ($NH_4OH$) as is often stated on the label. Thus aqueous ammonia solution is also a common base. Replacing a hydrogen atom of $NH_3$ with an alkyl group results in an amineAn organic compound that has the general formula $RNH_2$, where R is an alkyl group. Amines, like ammonia, are bases. ($RNH_2$), which is also a base. Amines have pungent odors—for example, methylamine ($CH_3NH_2$) is one of the compounds responsible for the foul odor associated with spoiled fish. The physiological importance of amines is suggested in the word *vitamin*, which is derived from the phrase *vital amines*. The word was coined to describe dietary substances that were effective at preventing scurvy, rickets, and other diseases because these substances were assumed to be amines. Subsequently, some vitamins have indeed been confirmed to be amines.

### Note the Pattern

Metal hydroxides (MOH) yield $OH^-$ ions and are bases, alcohols (ROH) do not yield $OH^-$ or $H^+$ ions and are neutral, and carboxylic acids ($RCO_2H$) yield $H^+$ ions and are acids.

### Summary

Common **acids** and the polyatomic anions derived from them have their own names and rules for nomenclature. The nomenclature of acids differentiates between **oxoacids**, in which the $H^+$ ion is attached to an oxygen atom of a polyatomic ion, and acids in which the $H^+$ ion is attached to another element. **Carboxylic acids** are an important class of organic acids. Ammonia is an important **base**, as are its organic derivatives, the **amines**.

### Key Takeaway

- Common acids and polyatomic anions derived from them have their own names and rules for nomenclature.

### Conceptual Problems

1. Name each acid.
    1. HCl
    2. $HBrO_3$
    3. $HNO_3$
    4. $H_2SO_4$
    5. $HIO_3$
2. Name each acid.
    1. HBr
    2. $H_2SO_3$
    3. $HClO_3$

4. HCN
5. $H_3PO_4$

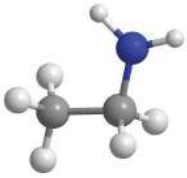
3. Name the aqueous acid that corresponds to each gaseous species.

1. hydrogen bromide
2. hydrogen cyanide
3. hydrogen iodide

4. For each structural formula, write the condensed formula and the name of the compound.

1. 
2. 

5. For each structural formula, write the condensed formula and the name of the compound.

1. 
2. 

6. When each compound is added to water, is the resulting solution acidic, neutral, or basic?

1. $CH_3CH_2OH$
2. $Mg(OH)_2$
3. $C_6H_5CO_2H$
4. LiOH
5. $C_3H_7CO_2H$
6. $H_2SO_4$

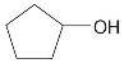
7. Draw the structure of the simplest example of each type of compound.

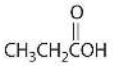
1. alkane
2. alkene
3. alkyne
4. aromatic hydrocarbon
5. alcohol
6. carboxylic acid
7. amine
8. cycloalkane

8. Identify the class of organic compound represented by each compound.

1. 
2. $CH_3CH_2OH$
3. HC≡CH


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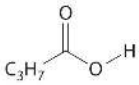
4. 
5. $C_3H_7NH_2$
6. $CH_3CH{=}CHCH_2CH_3$
7. 

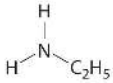
8. 

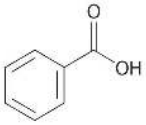

9. Identify the class of organic compound represented by each compound.

1. 

2. 

3. 
4. 
5. 

6. $CH_3C{\equiv}CH$
7. 

8. 


## Numerical Problems

1. Write the formula for each compound.
    1. hypochlorous acid
    2. perbromic acid
    3. hydrobromic acid
    4. sulfurous acid
    5. sodium perbromate
2. Write the formula for each compound.
    1. hydroiodic acid
    2. hydrogen sulfide
    3. phosphorous acid
    4. perchloric acid
    5. calcium hypobromite
3. Name each compound.
    1. HBr
    2. $H_2SO_3$
    3. HCN
    4. $HClO_4$

5. $NaHSO_4$

4. Name each compound.

1. $H_2SO_4$
2. $HNO_2$
3. $K_2HPO_4$
4. $H_3PO_3$
5. $Ca(H_2PO_4)_2 \cdot H_2O$

## Contributors

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Modified by Joshua Halpern

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# 4.7: Acid Base Reactions

**Learning Objectives**

- To know the characteristic properties of acids and bases

Acid–base reactions are essential in both biochemistry and industrial chemistry. Moreover, many of the substances we encounter in our homes, the supermarket, and the pharmacy are acids or bases. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. In fact, every amateur chef who has prepared mayonnaise or squeezed a wedge of lemon to marinate a piece of fish has carried out an acid–base reaction. Before we discuss the characteristics of such reactions, let's first describe some of the properties of acids and bases.

## Definitions of Acids and Bases

In Chapter 4.6, we defined **acids** as substances that dissolve in water to produce $H^+$ ions, whereas **bases** were defined as substances that dissolve in water to produce $OH^-$ ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ($CaCO_3$) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.




## The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce $H^+$ ions (protons; Equation 4.7.1 ), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide ($OH^-$) ions (Equation 4.7.2 ):

$$\underset{\text{an Arrhenius acid}}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{4.7.1}$$

$$\underset{\text{an Arrhenius base}}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{4.7.2}$$

According to Arrhenius, the characteristic properties of acids and bases are due exclusively to the presence of $H^+$ and $OH^-$ ions, respectively, in solution. Although Arrhenius's ideas were widely accepted, his definition of acids and bases had two major limitations:

1. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
2. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce $H^+$ and $OH^-$ ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation 4.7.3 ) is not an acid–base reaction because it does not involve $H^+$ and $OH^-$:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{4.7.3}$$

## The Brønsted–Lowry Definition of Acids and Bases

Because of the limitations of the Arrhenius definition, a more general definition of acids and bases was needed. One was proposed independently in 1923 by the Danish chemist J. N. Brønsted (1879–1947) and the British chemist T. M. Lowry (1874–1936), who defined acid–base reactions in terms of the transfer of a proton ($H^+$ ion) from one substance to another.

According to Brønsted and Lowry, an acid (A substance with at least one hydrogen atom that can dissociate to form an anion and an $H^+$ ion (a proton) in aqueous solution, thereby forming an acidic solution) is any substance that can donate a proton, and a base (a substance that produces one or more hydroxide ions ($OH^-$ and a cation when dissolved in aqueous solution, thereby forming a basic solution) is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton. Ammonia, for example, reacts with a proton to form $NH_4^+$, so in Equation 4.7.3, $NH_3$ is a Brønsted–Lowry base and $HCl$ is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified.

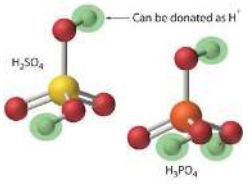
## Polyprotic Acids

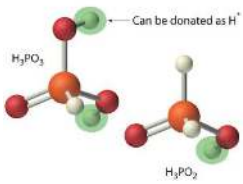
Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, $HNO_3$, and $HNO_2$. All carboxylic acids that contain a single $-CO_2H$ group, such as acetic acid ($CH_3CO_2H$), are monoprotic acids, dissociating to form $RCO_2^-$ and $H^+$ (section 4.6). A compound that can donate more than one proton per molecule. can donate more than one proton per molecule. For example, $H_2SO_4$ can donate two $H^+$ ions in separate steps, so it is a diprotic acid (a compound that can donate two protons per molecule in separate steps) and $H_3PO_4$, which is capable of donating three protons in successive steps, is a triprotic acid (a compound that can donate three protons per molecule in separate steps), (Equation 4.7.4, Equation 4.7.5, and Equation 4.7.6 ):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{8.7.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{8.7.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{8.7.6}$$



In chemical equations such as these, a double arrow is used to indicate that both the forward and reverse reactions occur simultaneously, so the forward reaction does not go to completion. Instead, the solution contains significant amounts of both reactants and products. Over time, the reaction reaches a state in which the concentration of each species in solution remains constant. The reaction is then said to be in equilibrium (the point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time).

## Strengths of Acids and Bases

We will not discuss the strengths of acids and bases quantitatively until next semester. Qualitatively, however, we can state that strong acids (An acid that reacts essentially completely with water) to give $H^+$ and the corresponding anion. react essentially completely with water to give $H^+$ and the corresponding anion. Similarly, strong bases (A base that dissociates essentially completely in water) to give $OH^-$ and the corresponding cation) dissociate essentially completely in water to give $OH^-$ and the corresponding cation. Strong acids and strong bases are both strong electrolytes. In contrast, only a fraction of the molecules of weak acids (An acid in which only a fraction of the molecules react with water) to producee $H^+$ and the corresponding anion. and weak bases (A base in which only a fraction of the molecules react with water to produce $OH^-$ and the corresponding cation) react with water to produce ions, so weak acids and weak bases are also weak electrolytes. Typically less than 5% of a weak electrolyte dissociates into ions in solution, whereas more than 95% is present in undissociated form.

In practice, only a few strong acids are commonly encountered: HCl, HBr, HI, $HNO_3$, $HClO_4$, and $H_2SO_4$ ($H_3PO_4$ is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are NaOH, KOH, and $Ca(OH)_2$. Common weak acids include HCN, $H_2S$, HF, oxoacids such as $HNO_2$ and HClO, and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{4.7.4}$$

Although acetic acid is *very* soluble in water, almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates), as we stated in section 4.1. Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 4.7.8 ) but a weak acid when it donates its second proton (Equation 8.7.9) as indicated by the single and double arrows, respectively:

$$\underset{strong\ acid}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{4.7.5}$$

$$\underset{weak\ acid}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{4.7.6}$$

Consequently, an aqueous solution of sulfuric acid contains $H^+_{(aq)}$ ions and a mixture of $HSO^-_{4\ (aq)}$ and $SO^{2-}_{4\ (aq)}$ ions, but no $H_2SO_4$ molecules.

The most common weak base is ammonia, which reacts with water to form small amounts of hydroxide ion:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{4.7.7}$$

Most of the ammonia (>99%) is present in the form of $NH_3$(g). Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as $S^{2-}$).

Table 4.7.1 lists some common strong acids and bases. Acids other than the six common strong acids are almost invariably weak acids. The only common strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba); any other bases you encounter are most likely weak. Remember that *there is no correlation between solubility and whether a substance is a strong or a weak electrolyte!* Many weak acids and bases are extremely soluble in water.

### Note the Pattern

There is *no* correlation between the solubility of a substance and whether it is a strong electrolyte, a weak electrolyte, or a nonelectrolyte.

Table 4.7.1 Common Strong Acids and Bases

| Strong Acids | | Strong Bases | |
|---|---|---|---|
| Hydrogen Halides | Oxoacids | Group 1 Hydroxides | Hydroxides of the Heavier Group 2 Elements |
| HCl | $HNO_3$ | LiOH | $Ca(OH)_2$ |
| HBr | $H_2SO_4$ | NaOH | $Sr(OH)_2$ |
| HI | $HClO_4$ | KOH | $Ba(OH)_2$ |
| | | RbOH | |
| | | CsOH | |

### Example 4.7.1

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

1. $CH_3CH_2CO_2H$
2. $CH_3OH$
3. $Sr(OH)_2$
4. $CH_3CH_2NH_2$
5. $HBrO_4$

**Given:** compound

**Asked for:** acid or base strength

**Strategy:**

**A** Determine whether the compound is organic or inorganic.

**B** If inorganic, determine whether the compound is acidic or basic by the presence of dissociable $H^+$ or $OH^-$ ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except $H_2SO_4$ are weak acids.

**Solution**

1. **A** This compound is propionic acid, which is organic. **B** It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
2. **A** $CH_3OH$ is methanol, an organic compound that contains the −OH group. **B** As a covalent compound, it does not dissociate to form the $OH^-$ ion. Because it does not contain a carboxylic acid ($-CO_2H$) group, methanol also cannot dissociate to form $H^+(aq)$ ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
3. **A** $Sr(OH)_2$ is an inorganic compound that contains one $Sr^{2+}$ and two $OH^-$ ions per formula unit. **B** We therefore expect it to be a strong base, similar to $Ca(OH)_2$.
4. **A** $CH_3CH_2NH_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 8.6.7), reacting with water to produce small amounts of the $OH^-$ ion. Ethylamine is therefore a weak base.
5. **A** $HBrO_4$ is perbromic acid, an inorganic compound. **B** It is not listed in Table 8.3 as one of the common strong acids, but that does not necessarily mean that it is a weak acid. If you examine the periodic table, you can see that Br lies directly below Cl in group 17. We might therefore expect that $HBrO_4$ is chemically similar to $HClO_4$, a strong acid—and, in fact, it is.

### Exercise 4.7.1

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

1. $Ba(OH)_2$

2. $HIO_4$
3. $CH_3CH_2CH_2CO_2H$
4. $(CH_3)_2NH$
5. $CH_2O$

**Answer**

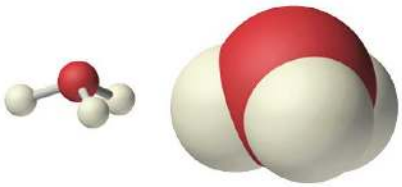
1. strong base
2. strong acid
3. weak acid
4. weak base
5. none of these; formaldehyde is a neutral molecule

## The Hydronium Ion

Because isolated protons are *very* unstable and hence very reactive, an acid never simply "loses" an $H^+$ ion. Instead, the proton is always transferred to another substance, which acts as a base in the Brønsted–Lowry definition. Thus in every acid–base reaction, one species acts as an acid and one species acts as a base. Occasionally, the same substance performs both roles, as you will see later. When a strong acid dissolves in water, the proton that is released is transferred to a water molecule that acts as a proton acceptor or base, as shown for the dissociation of sulfuric acid:

$$\underset{acid\ (proton\ donor)}{H_2SO_4(l)} + \underset{base\ (proton\ acceptor)}{H_2O(l)} \rightarrow \underset{acid}{H_3O^+(aq)} + \underset{base}{HSO_4^-(aq)} \tag{4.7.8}$$

Technically, therefore, it is imprecise to describe the dissociation of a strong acid as producing $H^+_{(aq)}$ ions, as we have been doing. The resulting $H_3O^+$ ion, called the hydronium ionis a more accurate representation of $H^+_{(aq)}$. For the sake of brevity, however, in discussing acid dissociation reactions, we often show the product as $H^+_{(aq)}$ (as in Equation 4.7.7 ) with the understanding that the product is actually the$H_3O^+_{(aq)}$ ion.




Conversely, bases that do not contain the hydroxide ion accept a proton from water, so small amounts of $OH^-$ are produced, as in the following:

$$\underset{base}{NH_3(g)} + \underset{acid}{H_2O(l)} \rightleftharpoons \underset{acid}{NH_4^+(aq)} + \underset{base}{OH^-(aq)}$$

Again, the double arrow indicates that the reaction does not go to completion but rather reaches a state of equilibrium. In this reaction, water acts as an acid by donating a proton to ammonia, and ammonia acts as a base by accepting a proton from water. Thus water can act as either an acid or a base by donating a proton to a base or by accepting a proton from an acid. Substances that can behave as both an acid and a base are said to be amphotericWhen substances can behave as both an acid and a base..

The products of an acid–base reaction are also an acid and a base. In Equation 4.7.11, for example, the products of the reaction are the hydronium ion, here an acid, and the hydrogen sulfate ion, here a weak base. In Equation 4.7.12, the products are $NH_4^+$, an acid, and $OH^-$, a base. The product $NH_4^+$ is called the conjugate acidThe substance formed when a Brønsted–Lowry base accepts a proton. of the base $NH_3$, and the product $OH^-$ is called the conjugate baseThe substance formed when a Brønsted–Lowry acid donates a proton. of the acid $H_2O$. Thus all acid–base reactions actually involve two conjugate acid–base pairsAn acid and a base that differ by only one hydrogen ion. All acid–base reactions involve two conjugate acid–base pairs, the Brønsted–Lowry acid and

the base it forms after donating its proton, and the Brønsted–Lowry base and the acid it forms after accepting a proton.; in Equation 4.7.12, they are $NH_4^+/NH_3$ and $H_2O/OH^-$.

## Neutralization Reactions

A neutralization reaction (a chemical reaction in which an acid and a base react in stoichiometric amounts to produce water and a salt) is one in which an acid and a base react in stoichiometric amounts to produce water and a salt (the general term for any ionic substance that does not have OH− as the anion or H+ as the cation), the general term for any ionic substance that does not have $OH^-$ as the anion or $H^+$ as the cation. If the base is a metal hydroxide, then the general formula for the reaction of an acid with a base is described as follows: *Acid plus base yields water plus salt*. For example, the reaction of equimolar amounts of HBr and NaOH to give water and a salt (NaBr) is a neutralization reaction:

$$\underset{acid}{HBr(aq)} + \underset{base}{NaOH(aq)} \rightarrow \underset{water}{H_2O(l)} + \underset{salt}{NaBr(aq)} \tag{4.7.9}$$

### Note the Pattern

Acid plus base yields water plus salt.

If we write the complete ionic equation for the reaction in Equation 4.7.13, we see that $Na^+_{(aq)}$ and $Br^-_{(aq)}$ are spectator ions and are not involved in the reaction:

$$H^+(aq) + \cancel{Br^-(aq)} + \cancel{Na^+(aq)} + OH^-(aq) \rightarrow H_2O(l) + \cancel{Na^+(aq)} + \cancel{Br^-(aq)} \tag{4.7.10}$$

The overall reaction is therefore simply the combination of $H^+$(aq) and $OH^-$(aq) to produce $H_2O$, as shown in the net ionic equation:

\[ H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \]

The net ionic equation for the reaction of any strong acid with any strong base is identical to Equation 4.7.15.

The strengths of the acid and the base generally determine whether the reaction goes to completion. The reaction of *any* strong acid with *any* strong base goes essentially to completion, as does the reaction of a strong acid with a weak base, and a weak acid with a strong base. Examples of the last two are as follows:

$$\underset{strong\ acid}{HCl(aq)} + \underset{weak\ base}{NH_3(aq)} \rightarrow \underset{salt}{NH_4Cl(aq)} \tag{4.7.11}$$

$$\underset{weak\ acid}{CH_3CO_2H(aq)} + \underset{strong\ base}{NaOH(aq)} \rightarrow \underset{salt}{CH_3CO_2Na(aq)} + H_2O(l) \tag{4.7.12}$$

Sodium acetate is written with the organic component first followed by the cation, as is usual for organic salts. Most reactions of a weak acid with a weak base also go essentially to completion. One example is the reaction of acetic acid with ammonia:

$$\underset{weak\ acid}{CH_3CO_2H(aq)} + \underset{weak\ base}{NH_3(aq)} \rightarrow \underset{salt}{CH_3CO_2NH_4(aq)} \tag{4.7.13}$$

An example of an acid–base reaction that does not go to completion is the reaction of a weak acid or a weak base with water, which is both an extremely weak acid and an extremely weak base. We will discuss these reactions in more detail in Chapter 16

### Note the Pattern

Except for the reaction of a weak acid or a weak base with water, acid–base reactions essentially go to completion.

In some cases, the reaction of an acid with an anion derived from a weak acid (such as $HS^-$) produces a gas (in this case, $H_2S$). Because the gaseous product escapes from solution in the form of bubbles, the reverse reaction cannot occur. Therefore, these reactions tend to be forced, or driven, to completion. Examples include reactions in which an acid is added to ionic compounds that contain the $HCO_3^-$, $CN^-$, or $S^{2-}$ anions, all of which are driven to completion (Figure 4.7.1 ):

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \tag{4.7.14}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l) \tag{4.7.15}$$

$$CN^-(aq) + H^+(aq) \rightarrow HCN(g) \tag{4.7.16}$$

$$S^{2-}(aq) + H^{+}(aq) \rightarrow HS^{-}(aq) \tag{4.7.17}$$

$$HS^{-}(aq) + H^{+}(aq) \rightarrow H_2S(g) \tag{4.7.18}$$




Figure 4.7.1 The Reaction of Dilute Aqueous HCl with a Solution of $Na_2CO_3$ *Note the vigorous formation of gaseous* $CO_2$.

The reactions in Equation 4.7.21 are responsible for the rotten egg smell that is produced when metal sulfides come in contact with acids.

### Example 4.7.2

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$] to give calcium propionate. Do you expect this reaction to go to completion, making it a feasible method for the preparation of calcium propionate?

**Given:** reactants and product

**Asked for:** balanced chemical equation and whether the reaction will go to completion

**Strategy:**

Write the balanced chemical equation for the reaction of propionic acid with calcium hydroxide. Based on their acid and base strengths, predict whether the reaction will go to completion.

**Solution**

Propionic acid is an organic compound that is a weak acid, and calcium hydroxide is an inorganic compound that is a strong base. The balanced chemical equation is as follows:

$$2CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + 2H_2O(l)$$

The reaction of a weak acid and a strong base will go to completion, so it is reasonable to prepare calcium propionate by mixing solutions of propionic acid and calcium hydroxide in a 2:1 mole ratio.

### Exercise 4.7.2

Write a balanced chemical equation for the reaction of solid sodium acetate with dilute sulfuric acid to give sodium sulfate.

**Answer**

$$2CH_3CO_2Na(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CH_3CO_2H(aq)$$



**Stomach acid.** An antacid tablet reacts with 0.1 M HCl (the approximate concentration found in the human stomach).

One of the most familiar and most heavily advertised applications of acid–base chemistry is *antacids*, which are bases that neutralize stomach acid. The human stomach contains an approximately 0.1 M solution of hydrochloric acid that helps digest foods. If the protective lining of the stomach breaks down, this acid can attack the stomach tissue, resulting in the formation of an *ulcer*. Because one factor that is believed to contribute to the formation of stomach ulcers is the production of excess acid in the stomach, many individuals routinely consume large quantities of antacids. The active ingredients in antacids include sodium bicarbonate and potassium bicarbonate ($NaHCO_3$ and $KHCO_3$; Alka-Seltzer); a mixture of magnesium hydroxide and aluminum hydroxide [$Mg(OH)_2$ and $Al(OH)_3$; Maalox, Mylanta]; calcium carbonate ($CaCO_3$; Tums); and a complex salt, dihydroxyaluminum sodium carbonate [$NaAl(OH)_2CO_3$; original Rolaids]. Each has certain advantages and disadvantages. For example, $Mg(OH)_2$ is a powerful laxative (it is the active ingredient in milk of magnesia), whereas $Al(OH)_3$ causes constipation. When mixed, each tends to counteract the unwanted effects of the other. Although all antacids contain both an anionic base ($OH^-$, $CO_3^{2-}$, or $HCO_3^-$) and an appropriate cation, they differ substantially in the amount of active ingredient in a given mass of product.

### ✔ Example 4.7.3

Assume that the stomach of someone suffering from acid indigestion contains 75 mL of 0.20 M HCl. How many Tums tablets are required to neutralize 90% of the stomach acid, if each tablet contains 500 mg of $CaCO_3$? (Neutralizing all of the stomach acid is not desirable because that would completely shut down digestion.)

**Given:** volume and molarity of acid and mass of base in an antacid tablet

**Asked for:** number of tablets required for 90% neutralization

**Strategy:**

**A** Write the balanced chemical equation for the reaction and then decide whether the reaction will go to completion.

**B** Calculate the number of moles of acid present. Multiply the number of moles by the percentage to obtain the quantity of acid that must be neutralized. Using mole ratios, calculate the number of moles of base required to neutralize the acid.

**C** Calculate the number of moles of base contained in one tablet by dividing the mass of base by the corresponding molar mass. Calculate the number of tablets required by dividing the moles of base by the moles contained in one tablet.

**Solution**

**A** We first write the balanced chemical equation for the reaction:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$$

Each carbonate ion can react with 2 mol of $H^+$ to produce $H_2CO_3$, which rapidly decomposes to $H_2O$ and $CO_2$. Because HCl is a strong acid and $CO_3^{2-}$ is a weak base, the reaction will go to completion.

**B** Next we need to determine the number of moles of HCl present:

$$75\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.20\ mol\ HCl}{\cancel{L}}\right) = 0.015\ mol\ HCl$$

Because we want to neutralize only 90% of the acid present, we multiply the number of moles of HCl by 0.90:

$$(0.015\ mol\ HCl)(0.90) = 0.014\ mol\ HCl$$

We know from the stoichiometry of the reaction that each mole of $CaCO_3$ reacts with 2 mol of HCl, so we need

$$moles\ CaCO_3 = 0.014\ \cancel{mol\ HCl}\left(\frac{1\ mol\ CaCO_3}{2\ \cancel{mol\ HCl}}\right) = 0.0070\ mol\ CaCO_3$$

**C** Each Tums tablet contains

$$\left(\frac{500\ \cancel{mg\ CaCO_3}}{1\ Tums\ tablet}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg\ CaCO_3}}\right)\left(\frac{1\ mol\ CaCO_3}{100.1\ \cancel{g}}\right) = 0.00500\ mol\ CaCO_3$$

Thus we need $\frac{0.0070\ \cancel{mol\ CaCO_3}}{0.00500\ \cancel{mol\ CaCO_3}} = 1.4$ Tums tablets.

**? Exercise 4.7.3**

Assume that as a result of overeating, a person's stomach contains 300 mL of 0.25 M HCl. How many Rolaids tablets must be consumed to neutralize 95% of the acid, if each tablet contains 400 mg of $NaAl(OH)_2CO_3$? The neutralization reaction can be written as follows:

$$NaAl(OH)_2CO_3(s) + 4HCl(aq) \rightarrow AlCl_3(aq) + NaCl(aq) + CO_2(g) + 3H_2O(l)$$

**Answer**

6.4 tablets

## The pH Scale

One of the key factors affecting reactions that occur in dilute solutions of acids and bases is the concentration of $H^+$ and $OH^-$ ions. The pH scaleA logarithmic scale used to express the hydrogen ion ($H^+$) concentration of a solution, making it possible to describe acidity or basicity quantitatively. provides a convenient way of expressing the hydrogen ion ($H^+$) concentration of a solution and enables us to describe acidity or basicity in quantitative terms.

Pure liquid water contains extremely low but measurable concentrations of $H_3O^+$(aq) and $OH^-$(aq) ions produced via an *autoionization reaction*, in which water acts simultaneously as an acid and as a base:

\[H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)\tag{8.7.22}\]

The concentration of hydrogen ions in pure water is only $1.0 \times 10^{-7}$ M at 25°C. Because the autoionization reaction produces both a proton and a hydroxide ion, the $OH^-$ concentration in pure water is also $1.0 \times 10^{-7}$ M. Pure water is a neutral solutionA solution in which the total positive charge from all the cations is matched by an identical total negative charge from all the anions., in which $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M.

The pH scale describes the hydrogen ion concentration of a solution in a way that avoids the use of exponential notation; pHThe negative base-10 logarithm of the hydrogen ion concentration: $pH=-log[H^+]$ is defined as the negative base-10 logarithm of the hydrogen ion concentration:*pH* is actually defined as the negative base-10 logarithm of hydrogen ion *activity*. As you will learn in a more advanced course, the activity of a substance in solution is related to its concentration. For dilute solutions such as those we are discussing, the activity and the concentration are approximately the same.

$$pH = -log[H^+] \tag{4.7.19}$$

Conversely,

\([ [H^+] = 10^{-pH}\]

Because the hydrogen ion concentration is $1.0 \times 10^{-7}$ M in pure water at 25°C, the pH of pure liquid water (and, by extension, of any neutral solution) is

$$pH = -log[1.0 \times 10^{-7}] = 7.00 \tag{4.7.20}$$

Adding an acid to pure water increases the hydrogen ion concentration and decreases the hydroxide ion concentration because a neutralization reaction occurs, such as that shown in Equation 8.7.15. Because the negative exponent of $[H^+]$ becomes smaller as $[H^+]$ increases, the pH *decreases* with increasing $[H^+]$. For example, a 1.0 M solution of a strong monoprotic acid such as HCl or $HNO_3$ has a pH of 0.00:

$$pH = -log[1.0] = 0.00 \tag{4.7.21}$$

### Note the Pattern

pH decreases with increasing $[H^+]$.

Conversely, adding a base to pure water increases the hydroxide ion concentration and decreases the hydrogen ion concentration. Because the autoionization reaction of water does not go to completion, neither does the neutralization reaction. Even a strongly basic solution contains a detectable amount of $H^+$ ions. For example, a 1.0 M $OH^-$ solution has $[H^+] = 1.0 \times 10^{-14}$ M. The pH of a 1.0 M NaOH solution is therefore

$$pH = -log[1.0 \times 10^{-14}] = 14.00 \tag{4.7.22}$$

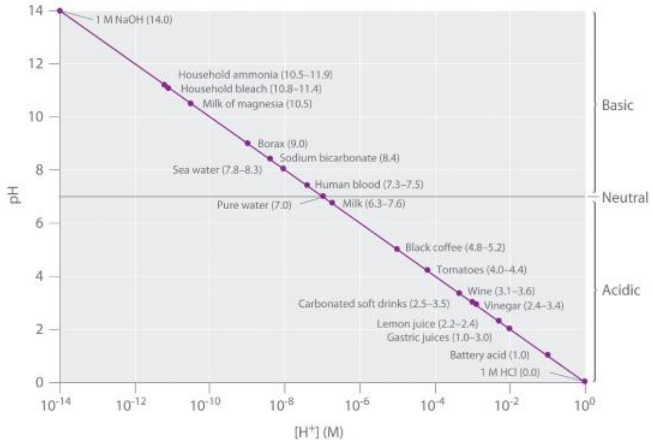
For practical purposes, the pH scale runs from pH = 0 (corresponding to 1 M $H^+$) to pH 14 (corresponding to 1 M $OH^-$), although pH values less than 0 or greater than 14 are possible.

We can summarize the relationships between acidity, basicity, and pH as follows:

- If pH = 7.0, the solution is neutral.
- If pH < 7.0, the solution is acidic.
- If pH > 7.0, the solution is basic.

Keep in mind that the pH scale is logarithmic, so a change of 1.0 in the pH of a solution corresponds to a *tenfold* change in the hydrogen ion concentration. The foods and consumer products we encounter daily represent a wide range of pH values, as shown in Figure 8.7.2.

**Figure 8.7.2 A Plot of pH versus $[H^+]$ for Some Common Aqueous Solutions**




*Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.*

### Example 4.7.4

1. What is the pH of a $2.1 \times 10^{-2}$ M aqueous solution of $HClO_4$?
2. The pH of a vinegar sample is 3.80. What is its hydrogen ion concentration?

**Given:** molarity of acid or pH

**Asked for:** pH or $[H^+]$

**Strategy:**

Using the balanced chemical equation for the acid dissociation reaction and Equation 4.7.24 or 4.7.25, determine $[H^+]$ and convert it to pH or vice versa.

**Solution**

1. $HClO_4$ (perchloric acid) is a strong acid, so it dissociates completely into $H^+$ ions and $ClO_4^-$ ions:

$$HClO_4(l) \rightarrow H^+(aq) + ClO_4^-(aq)$$

The $H^+$ ion concentration is therefore the same as the perchloric acid concentration. The pH of the perchloric acid solution is thus

$$pH = -log[H^+] = -log(2.1 \times 10^{-2}) = 1.68$$

The result makes sense: the $H^+$ ion concentration is between $10^{-1}$ M and $10^{-2}$ M, so the pH must be between 1 and 2.

*Note*: The assumption that $[H^+]$ is the same as the concentration of the acid is valid for *only* strong acids. Because weak acids do *not* dissociate completely in aqueous solution, a more complex procedure is needed to calculate the pH of their solutions.

2. We are given the pH and asked to calculate the hydrogen ion concentration. From Equation 4.7.24,

$$10^{-pH} = [H^+]$$

Thus $[H^+] = 10^{-3.80} = 1.6 \times 10^{-4}\ M$.

## Exercise 4.7.4

1. What is the pH of a $3.0 \times 10^{-5}$ M aqueous solution of $HNO_3$?
2. What is the hydrogen ion concentration of turnip juice, which has a pH of 5.41?

**Answer**

1. $pH = 4.52$
2. $[H^+] = 3.9 \times 10^{-6}\ M$

Tools have been developed that make the measurement of pH simple and convenient (Figure 8.6.3). For example, pH paper consists of strips of paper impregnated with one or more acid–base indicatorsAn intensely colored organic molecule whose color changes dramatically depending on the pH of the solution., which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the $H^+$ ion concentration.

Figure 8.6.3 Two Ways of Measuring the pH of a Solution: pH Paper and a pH Meter

Note that both show that the pH is 1.7, but the pH meter gives a more precise value.

## Key Equations

**definition of pH**

Equation 4.7.231 : $pH = -log[H^+]$

Equation 4.7.24 : $[H^+] = 10^{-pH}$

## Summary

Acid–base reactions require both an acid and a base. In Brønsted–Lowry terms, an **acid** is a substance that can donate a proton ($H^+$), and a **base** is a substance that can accept a proton. All acid–base reactions contain two acid–base pairs: the reactants and the products. Acids can donate one proton (**monoprotic acids**), two protons (**diprotic acids**), or three protons (**triprotic acids**).

Compounds that are capable of donating more than one proton are generally called **polyprotic acids**. Acids also differ in their tendency to donate a proton, a measure of their acid strength. **Strong acids** react completely with water to produce $H_3O^+(aq)$ (the **hydronium ion**), whereas **weak acids** dissociate only partially in water. Conversely, **strong bases** react completely with water to produce the hydroxide ion, whereas **weak bases** react only partially with water to form hydroxide ions. The reaction of a strong acid with a strong base is a **neutralization reaction**, which produces water plus a **salt**.

The acidity or basicity of an aqueous solution is described quantitatively using the **pH scale**. The **pH** of a solution is the negative logarithm of the $H^+$ ion concentration and typically ranges from 0 for strongly acidic solutions to 14 for strongly basic ones. Because of the *autoionization reaction* of water, which produces small amounts of hydronium ions and hydroxide ions, a **neutral solution** of water contains $1 \times 10^{-7}$ M $H^+$ ions and has a pH of 7.0. An **indicator** is an intensely colored organic substance whose color is pH dependent; it is used to determine the pH of a solution.

## Key Takeaway

- An acidic solution and a basic solution react together in a neutralization reaction that also forms a salt.

## Conceptual Problems

1. Why was it necessary to expand on the Arrhenius definition of an acid and a base? What specific point does the Brønsted–Lowry definition address?
2. State whether each compound is an acid, a base, or a salt.
   a. $CaCO_3$
   b. $NaHCO_3$
   c. $H_2SO_4$
   d. $CaCl_2$
   e. $Ba(OH)_2$
3. State whether each compound is an acid, a base, or a salt.
   a. $NH_3$
   b. $NH_4Cl$
   c. $H_2CO_3$
   d. $CH_3COOH$
   e. NaOH
4. Classify each compound as a strong acid, a weak acid, a strong base, or a weak base in aqueous solution.
   a. sodium hydroxide
   b. acetic acid
   c. magnesium hydroxide
   d. tartaric acid
   e. sulfuric acid
   f. ammonia
   g. hydroxylamine ($NH_2OH$)
   h. hydrocyanic acid
5. Decide whether each compound forms an aqueous solution that is strongly acidic, weakly acidic, strongly basic, or weakly basic.
   a. propanoic acid
   b. hydrobromic acid
   c. methylamine
   d. lithium hydroxide
   e. citric acid
   f. sodium acetate
   g. ammonium chloride

h. barium hydroxide

6. What is the relationship between the strength of an acid and the strength of the conjugate base derived from that acid? Would you expect the $CH_3CO_2^-$ ion to be a strong base or a weak base? Why? Is the hydronium ion a strong acid or a weak acid? Explain your answer.
7. What are the products of an acid–base reaction? Under what circumstances is one of the products a gas?
8. Explain how an aqueous solution that is strongly basic can have a pH, which is a measure of the *acidity* of a solution.

### Answer

1.
2.
3.
4.
5. a. weakly acidic
   b. strongly acidic
   c. weakly basic
   d. strongly basic
   e. weakly acidic
   f. weakly basic
   g. weakly acidic
   h. strongly basic
6.
7.
8.

### Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 3 (section 4.11")before proceeding to the Numerical Problems.*

1. Derive an equation to relate the hydrogen ion concentration to the molarity of a solution of a strong monoprotic acid.
2. Derive an equation to relate the hydroxide ion concentration to the molarity of a solution of
   a. a group I hydroxide.
   b. a group II hydroxide.
3. Given the following salts, identify the acid and the base in the neutralization reactions and then write the complete ionic equation:
   a. barium sulfate
   b. lithium nitrate
   c. sodium bromide
   d. calcium perchlorate
4. What is the pH of each solution?
   a. $5.8 \times 10^{-3}$ mol of $HNO_3$ in 257 mL of water
   b. 0.0079 mol of HI in 750 mL of water
   c. 0.011 mol of $HClO_4$ in 500 mL of water
   d. 0.257 mol of HBr in 5.00 L of water
5. What is the hydrogen ion concentration of each substance in the indicated pH range?
   a. black coffee (pH 5.10)
   b. milk (pH 6.30–7.60)
   c. tomatoes (pH 4.00–4.40)

6. What is the hydrogen ion concentration of each substance in the indicated pH range?
    a. orange juice (pH 3–4)
    b. fresh egg white (pH 7.60–7.80)
    c. lemon juice (pH 2.20–2.40)
7. What is the pH of a solution prepared by diluting 25.00 mL of 0.879 M HCl to a volume of 555 mL?
8. Vinegar is primarily an aqueous solution of acetic acid. Commercial vinegar typically contains 5.0 g of acetic acid in 95.0 g of water. What is the concentration of commercial vinegar? If only 3.1% of the acetic acid dissociates to $CH_3CO_2^-$ and $H^+$, what is the pH of the solution? (Assume the density of the solution is 1.00 g/mL.)
9. If a typical household cleanser is 0.50 M in strong base, what volume of 0.998 M strong monoprotic acid is needed to neutralize 50.0 mL of the cleanser?
10. A 25.00 mL sample of a 0.9005 M solution of HCl is diluted to 500.0 mL. What is the molarity of the final solution? How many milliliters of 0.223 M NaOH are needed to neutralize 25.00 mL of this final solution?
11. If 20.0 mL of 0.10 M NaOH are needed to neutralize 15.0 mL of gastric fluid, what is the molarity of HCl in the fluid? (Assume all the acidity is due to the presence of HCl.) What other base might be used instead of NaOH?
12. Malonic acid ($C_3H_4O_4$) is a diprotic acid used in the manufacture of barbiturates. How many grams of malonic acid are in a 25.00 mL sample that requires 32.68 mL of 1.124 M KOH for complete neutralization to occur? Malonic acid is a dicarboxylic acid; propose a structure for malonic acid.
13. Describe how you would prepare 500 mL of a 1.00 M stock solution of HCl from an HCl solution that is 12.11 M. Using your stock solution, how would you prepare 500 mL of a solution that is 0.012 M in HCl?
14. Given a stock solution that is 8.52 M in HBr, describe how you would prepare a 500 mL solution with each concentration.
    a. 2.50 M
    b. $4.00 \times 10^{-3}$ M
    c. 0.989 M
15. How many moles of solute are contained in each?
    a. 25.00 mL of 1.86 M NaOH
    b. 50.00 mL of 0.0898 M HCl
    c. 13.89 mL of 0.102 M HBr
16. A chemist needed a solution that was approximately 0.5 M in HCl but could measure only 10.00 mL samples into a 50.00 mL volumetric flask. Propose a method for preparing the solution. (Assume that concentrated HCl is 12.0 M.)
17. Write the balanced chemical equation for each reaction.
    a. perchloric acid with potassium hydroxide
    b. nitric acid with calcium hydroxide
18. Write the balanced chemical equation for each reaction.
    a. solid strontium hydroxide with hydrobromic acid
    b. aqueous sulfuric acid with solid sodium hydroxide
19. A neutralization reaction gives calcium nitrate as one of the two products. Identify the acid and the base in this reaction. What is the second product? If the product had been cesium iodide, what would have been the acid and the base? What is the complete ionic equation for each reaction?

## Answers

1. $[H_3O^+] = [HA]$ M
2. 
3. a. $H_2SO_4$ and $Ba(OH)_2$; $2H^+ + SO_4^{2-} + Ba^{2+} + 2OH^- \rightarrow 2H_2O + Ba^{2+} + SO_4^{2-}$

b. $HNO_3$ and LiOH; $H^+ + NO_3^- + Li^+ + OH^- \rightarrow H_2O + Li^+ + NO_3^-$
c. HBr and NaOH; $H^+ + Br^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Br^-$
d. $HClO_4$ and $Ca(OH)_2$; $2H^+ + 2ClO_4^- + Ca^{2+} + 2OH^- \rightarrow 2H_2O + Ca^{2+} + 2ClO_4^-$

4.

5. a. $7.9 \times 10^{-6}$ M $H^+$
b. $5.0 \times 10^{-7}$ to $2.5 \times 10^{-8}$ M $H^+$
c. $1.0 \times 10^{-4}$ to $4.0 \times 10^{-5}$ M $H^+$

6.

7. pH = 1.402

8.

9. 25 mL

10.

11. 0.13 M HCl; magnesium carbonate, $MgCO_3$, or aluminum hydroxide, $Al(OH)_3$

12.

13. 1.00 M solution: dilute 41.20 mL of the concentrated solution to a final volume of 500 mL. 0.012 M solution: dilute 12.0 mL of the 1.00 M stock solution to a final volume of 500 mL.

14.

15. a. $4.65 \times 10^{-2}$ mol NaOH
b. $4.49 \times 10^{-3}$ mol HCl
c. $1.42 \times 10^{-3}$ mol HBr

16.

17. a. $HClO_4 + KOH \rightarrow KClO_4 + H_2O$
b. $2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$

18.

19. The acid is nitric acid, and the base is calcium hydroxide. The other product is water.

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

The acid is hydroiodic acid, and the base is cesium hydroxide. The other product is water.

$$HI + CsOH \rightarrow CsI + H_2O$$

The complete ionic equations are

$$2H^+ + 2NO_3^- + Ca^{2+} + 2OH^- \rightarrow Ca^{2+} + 2NO_3^- + H_2O$$
$$H^+ + I^- + Cs^+ + OH^- \rightarrow Cs^+ + I^- + H_2O$$

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# 4.8: The Chemistry of Acid Rain

**Learning Objectives**

- To understand the chemistry of acid rain.

Acid–base reactions can have a strong environmental impact. For example, a dramatic increase in the acidity of rain and snow over the past 150 years is dissolving marble and limestone surfaces, accelerating the corrosion of metal objects, and decreasing the pH of natural waters. This environmental problem is called acid rainPrecipitation that is dramatically more acidic because of human activities. and has significant consequences for all living organisms. To understand acid rain requires an understanding of acid–base reactions in aqueous solution.

The term *acid rain* is actually somewhat misleading because even pure rainwater collected in areas remote from civilization is slightly acidic (pH ≈ 5.6) due to dissolved carbon dioxide, which reacts with water to give carbonic acid, a weak acid:

$$CO_2\,(g) + H_2O\,(l) \;\rightleftharpoons\; H_2CO_3\,(aq) \;\rightleftharpoons\; H^+\,(aq) + HCO_3^-\,(aq)$$

The English chemist Robert Angus Smith is generally credited with coining the phrase *acid rain* in 1872 to describe the increased acidity of the rain in British industrial centers (such as Manchester), which was apparently caused by the unbridled excesses of the early Industrial Revolution, although the connection was not yet understood. At that time, there was no good way to measure hydrogen ion concentrations, so it is difficult to know the actual pH of the rain observed by Smith. Typical pH values for rain in the continental United States now range from 4 to 4.5, with values as low as 2.0 reported for areas such as Los Angeles. Recall from Figure 4.8.1 that rain with a pH of 2 is comparable in acidity to lemon juice, and even “normal” rain is now as acidic as tomato juice or black coffee.

What is the source of the increased acidity in rain and snow? Chemical analysis shows the presence of large quantities of sulfate ($SO_4^{2-}$) and nitrate ($NO_3^-$) ions, and a wide variety of evidence indicates that a significant fraction of these species come from nitrogen and sulfur oxides produced during the combustion of fossil fuels. At the high temperatures found in both internal combustion engines and lightning discharges, molecular nitrogen and molecular oxygen react to give nitric oxide:

$$N_2\,(g) + O_2\,(g) \;\rightarrow\; 2NO\,(g) \tag{4.8.1}$$

Nitric oxide then reacts rapidly with excess oxygen to give nitrogen dioxide, the compound responsible for the brown color of smog:

$$2NO\,(g) + O_2\,(g) \;\rightarrow\; 2NO_2\,(g) \tag{4.8.2}$$

When nitrogen dioxide dissolves in water, it forms a 1:1 mixture of nitrous acid and nitric acid:

$$2NO_2\,(g) + H_2O\,(l) \;\rightarrow\; HNO_2\,(aq) + HNO_3\,(aq) \tag{4.8.3}$$

Because molecular oxygen eventually oxidizes nitrous acid to nitric acid, the overall reaction is

$$2N_2\,(g) + 5O_2\,(g) + 2H_2O\,(l) \;\rightarrow 4HNO_3(aq) \tag{4.8.4}$$

Large amounts of sulfur dioxide have always been released into the atmosphere by natural sources, such as volcanoes, forest fires, and the microbial decay of organic materials, but for most of Earth’s recorded history the natural cycling of sulfur from the atmosphere into oceans and rocks kept the acidity of rain and snow in check. Unfortunately, the burning of fossil fuels seems to have tipped the balance. Many coals contain as much as 5%–6% pyrite ($FeS_2$) by mass, and fuel oils typically contain at least 0.5% sulfur by mass. Since the mid-19th century, these fuels have been burned on a huge scale to supply the energy needs of our modern industrial society, releasing tens of millions of tons of additional $SO_2$ into the atmosphere annually. In addition, roasting sulfide ores to obtain metals such as zinc and copper produces large amounts of $SO_2$ via reactions such as

$$2ZnS\,(s) + 3O_2\,(g) \;\rightarrow 2ZnO\,(s) + 2SO_2\,(g) \tag{4.8.5}$$

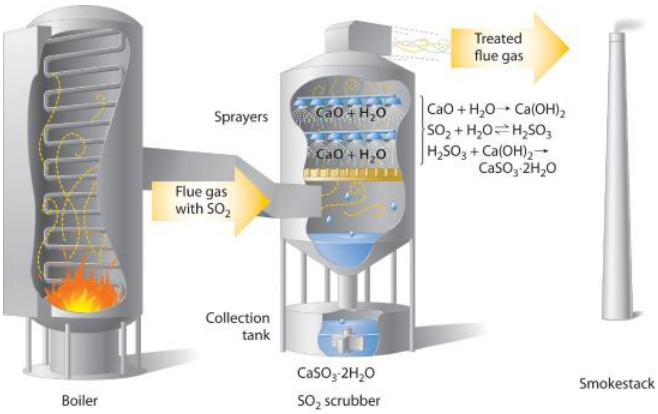
Regardless of the source, the $SO_2$ dissolves in rainwater to give sulfurous acid (Equation 8.8.7), which is eventually oxidized by oxygen to sulfuric acid (Equation 8.8.8):

$$SO_2\,(g) + H_2O\,(l) \;\rightarrow H_2SO_3(aq) \tag{4.8.6}$$

$$2H_2SO_3(aq) + O_2\,(g) \rightarrow 2H_2SO_4(aq) \tag{4.8.7}$$

Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of $SO_2$ and NO. For example, coal-burning power plants now use $SO_2$ "scrubbers," which trap $SO_2$ by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($CaSO_3{\cdot}2H_2O$; Figure 4.8.1 ).

Figure 4.8.1 Schematic Diagram of a Wet Scrubber System




*In coal-burning power plants, $SO_2$ can be removed ("scrubbed") from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($CaSO_3{\cdot}2H_2O$). Removing $SO_2$ from the gases prevents its conversion to $SO_3$ and subsequent reaction with rainwater (acid rain). Scrubbing systems are now commonly used to minimize the environmental effects of large-scale fossil fuel combustion.*

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate ($CaCO_3$), a salt derived from the weak acid $H_2CO_3$. As we saw in Section 4.7 the reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

$$CaCO_3\,(s) + H_2SO_4(aq) \rightarrow CaSO_4\,(s) + H_2O\,(l) + CO_2\,(g) \tag{4.8.8}$$

Because $CaSO_4$ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone. The Lincoln Memorial in Washington, DC, which was built in 1922, already shows significant damage from acid rain, and many older objects are exhibiting even greater damage (Figure 4.8.2 ). Metal objects can also suffer damage from acid rain through oxidation–reduction reactions, which are discussed in Section 8.9 .

Figure 4.8.2 Acid Rain Damage to a Statue of George Washington



*Both marble and limestone consist of $CaCO_3$, which reacts with acid rain in an acid–base reaction to produce $CaSO_4$. Because $CaSO_4$ is somewhat soluble in water, significant damage to the structure can result.*

The biological effects of acid rain are more complex. As indicated in Figure 4.8.2, biological fluids, such as blood, have a pH of 7–8. Organisms such as fish can maintain their internal pH in water that has a pH in the range of 6.5–8.5. If the external pH is too low, however, many aquatic organisms can no longer maintain their internal pH, so they die. A pH of 4 or lower is fatal for virtually all fish, most invertebrate animals, and many microorganisms. As a result of acid rain, the pH of some lakes in Europe and the United States has dropped below 4. Recent surveys suggest that up to 6% of the lakes in the Adirondack Mountains of upstate New York and 4% of the lakes in Sweden and Norway are essentially dead and contain no fish. Neither location contains large concentrations of industry, but New York lies downwind of the industrial Midwest, and Scandinavia is downwind of the most industrialized regions of western Europe. Both regions appear to have borne the brunt of the pollution produced by their upwind neighbors. One possible way to counter the effects of acid rain in isolated lakes is by adding large quantities of finely ground limestone, which neutralizes the acid via reaction.

A second major way in which acid rain can cause biological damage is less direct. Trees and many other plants are sensitive to the presence of aluminum and other metals in groundwater. Under normal circumstances, aluminum hydroxide [$Al(OH)_3$], which is present in some soils, is insoluble. At lower pH values, however, $Al(OH)_3$ dissolves via the following reaction:

$$Al(OH)_3\,(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O\,(l) \tag{4.8.9}$$

The result is increased levels of $Al^{3+}$ ions in groundwater. Because the $Al^{3+}$ ion is toxic to plants, high concentrations can affect plant growth. Acid rain can also weaken the leaves and roots of plants so much that the plants are unable to withstand other stresses. The combination of the two effects can cause significant damage to established forests, such as the Black Forest in Germany and the forests of the northeastern United States and Canada and other countries (Figure 4.8.3 ).

Figure 4.8.3 Acid Rain Damage to a Forest in the Czech Republic



*Trees and many other plants are sensitive to aluminum and other metals in groundwater. Acid rain increases the concentration of $Al^{3+}$ in groundwater, thereby adversely affecting plant growth. Large sections of established forests have been severely damaged.*

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# 4.9: Quantitative Analysis Using Titration

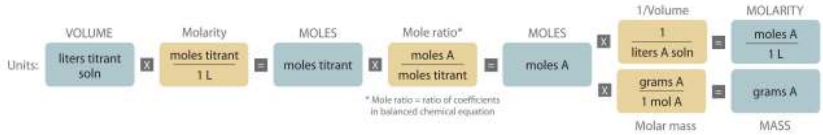
**Learning Objectives**

- To use titration methods to analyze solutions quantitatively.

To determine the amounts or concentrations of substances present in a sample, chemists use a combination of chemical reactions and stoichiometric calculations in a methodology called quantitative analysisA methodology that combines chemical reactions and stoichiometric calculations to determine the amounts or concentrations of substances present in a sample.. Suppose, for example, we know the identity of a certain compound in a solution but not its concentration. If the compound reacts rapidly and completely with another reactant, we may be able to use the reaction to determine the concentration of the compound of interest. In a titrationAn experimental procedure in which a carefully measured volume of a solution of known concentration is added to a measured volume of a solution containing a compound whose concentration is to be determined., a carefully measured volume of a solution of known concentration, called the titrantThe solution of known concentration that is reacted with a compound in a solution of unknown concentration in a titration., is added to a measured volume of a solution containing a compound whose concentration is to be determined (the *unknown*). The reaction used in a titration can be an acid–base reaction, a precipitation reaction, or an oxidation–reduction reaction. In all cases, the reaction chosen for the analysis must be fast, complete, and *specific*; that is, *only* the compound of interest should react with the titrant. The equivalence pointThe point in a titration where a stoichiometric amount (i.e., the amount required to react completely with the unknown) of the titrant has been added. is reached when a stoichiometric amount of the titrant has been added—the amount required to react completely with the unknown.

## Determining the Concentration of an Unknown Solution Using a Titration

The chemical nature of the species present in the unknown dictates which type of reaction is most appropriate and also how to determine the equivalence point. The volume of titrant added, its concentration, and the coefficients from the balanced chemical equation for the reaction allow us to calculate the total number of moles of the unknown in the original solution. Because we have measured the volume of the solution that contains the unknown, we can calculate the molarity of the unknown substance. This procedure is summarized graphically here:




**Example 4.9.1**

The calcium salt of oxalic acid [$Ca(O_2CCO_2)$] is found in the sap and leaves of some vegetables, including spinach and rhubarb, and in many ornamental plants. Because oxalic acid and its salts are toxic, when a food such as rhubarb is processed commercially, the leaves must be removed, and the oxalate content carefully monitored.

The reaction of $MnO_4^-$ with oxalic acid ($HO_2CCO_2H$) in acidic aqueous solution produces $Mn^{2+}$ and $CO_2$:

$$\underset{purple}{MnO_4^-\,(aq) + HO_2CCO_2H\,(aq)} \rightarrow \underset{colorless}{Mn^{2+}\,(aq)} + CO_2\,(g) + H_2O\,(l)$$

Because this reaction is rapid and goes to completion, potassium permanganate ($KMnO_4$) is widely used as a reactant for determining the concentration of oxalic acid. The following video demonstrates the reaction

Figure 4.9.1 *Redox reaction of potassium permanganate and oxalic acid*




Suppose you stirred a 10.0 g sample of canned rhubarb with enough dilute $H_2SO_4$(aq) to obtain 127 mL of colorless solution. Because the added permanganate is rapidly consumed, adding small volumes of a 0.0247 M $KMnO_4$ solution, which has a deep purple color, to the rhubarb extract does not initially change the color of the extract. When 15.4 mL of the permanganate solution have been added, however, the solution becomes a faint purple due to the presence of a slight excess of permanganate (Figure 8.9.1). If we assume that oxalic acid is the only species in solution that reacts with permanganate, what percentage of the mass of the original sample was calcium oxalate? The video below demonstrates the titration when small, measured amounts of a known permaganate solution are added. At the endpoint, the number of moles of permaganage added equals the number of moles of oxalate in the solution, thus determining how many moles of oxalate we started with

**Figure 8.9.2 Titration of a permaganate solution with oxalic acid**




*As oxalic asci is added to the potassium permaginate solution the purple color a disappears as the permanganate is consumed. As more permanganate is added, eventually all the oxalate is oxidized, and a faint purple color from the presence of excess permanganate appears, marking the endpoint .*

**Given:** equation, mass of sample, volume of solution, and molarity and volume of titrant

**Asked for:** mass percentage of unknown in sample

**Strategy:**

**A** Balance the chemical equation for the reaction using oxidation states.

**B** Calculate the number of moles of permanganate consumed by multiplying the volume of the titrant by its molarity. Then calculate the number of moles of oxalate in the solution by multiplying by the ratio of the coefficients in the balanced chemical equation. Because calcium oxalate contains a 1:1 ratio of $Ca^{2+}$:$^{-}O_2CCO_2^{-}$, the number of moles of oxalate in the solution is the same as the number of moles of calcium oxalate in the original sample.

**C** Find the mass of calcium oxalate by multiplying the number of moles of calcium oxalate in the sample by its molar mass. Divide the mass of calcium oxalate by the mass of the sample and convert to a percentage to calculate the percentage by mass of calcium oxalate in the original sample.

**Solution**

**A** As in all other problems of this type, the first requirement is a balanced chemical equation for the reaction. Using oxidation states gives

$$2MnO_4^-(aq) + 5HO_2CCO_2H(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Thus each mole of $MnO_4^-$ added consumes 2.5 mol of oxalic acid.

**B** Because we know the concentration of permanganate (0.0247 M) and the volume of permanganate solution that was needed to consume all the oxalic acid (15.4 mL), we can calculate the number of moles of $MnO_4^-$ consumed. To do this we first convert the volume in mL to a volume in liters. Then simply multiplying the molarity of the solution by the volume in liters we find the number of moles of $MnO_4^-$

$$15.4 \ \cancel{mL} \left(\frac{1 \ \cancel{L}}{1000 \ \cancel{mL}}\right)\left(\frac{0.0247 \ mol \ MnO_4^-}{1 \ \cancel{L}}\right) = 3.80 \times 10^4 \ mol \ MnO_4^-$$

The number of moles of oxalic acid, and thus oxalate, present can be calculated from the mole ratio of the reactants in the balanced chemical equation. We can abbreviate the table needed to calculate the number of moles of oxalic acid in the

$$moles \ HO_2CCO_2H = 3.80 \times 10^{-4} \ \cancel{mol \ MnO_4^-}\left(\frac{5 \ mol \ HO_2CCO_2H}{2 \ \cancel{mol \ MnO_4^-}}\right)$$
$$= 9.50 \times 10^{-4} \ mol \ HO_2CCO_2H$$

**C** The problem asks for the *percentage* of calcium oxalate by mass in the original 10.0 g sample of rhubarb, so we need to know the mass of calcium oxalate that produced $9.50 \times 10^{-4}$ mol of oxalic acid. Because calcium oxalate is $Ca(O_2CCO_2)$, 1 mol of calcium oxalate gave 1 mol of oxalic acid in the initial acid extraction:

$$Ca(O_2CCO_2)(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + HO_2CCO_2H(aq)$$

The mass of calcium oxalate originally present was thus

$$mass \ of \ CaC_2O_4 = 9.50 \times 10^{-4} \ \cancel{mol \ HO_2CCO_2H}\left(\frac{1 \ \cancel{mol \ CaC_2O_4}}{1 \ \cancel{mol \ HO_2CCO_2H}}\right)\left(\frac{128.10 \ g \ CaC_2O_4}{1 \ \cancel{mol \ CaC_2O_4}}\right)$$
$$= 0.122 \ g \ CaC_2O_4$$

The original sample contained 0.122 g of calcium oxalate per 10.0 g of rhubarb. The percentage of calcium oxalate by mass was thus

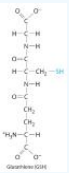
$$\%CaC_2O_4 = \frac{0.122 \ g}{10.0 \ g} \times 100 = 1.22\%$$

Because the problem asked for the percentage by mass of calcium oxalate in the original sample rather than for the *concentration* of oxalic acid in the extract, we do not need to know the volume of the oxalic acid solution for this calculation.

Add text here.

## ? Exercise 4.9.1

Glutathione is a low-molecular-weight compound found in living cells that is produced naturally by the liver. Health-care providers give glutathione intravenously to prevent side effects of chemotherapy and to prevent kidney problems after heart bypass surgery. Its structure is as follows:



Glutathione is found in two forms: one abbreviated as GSH (indicating the presence of an –SH group) and the other as GSSG (the *disulfide* form, in which an S–S bond links two glutathione units). The GSH form is easily oxidized to GSSG by elemental iodine:

$$2GSH(aq) + I_2(aq) \rightarrow GSSG(aq) + 2HI(aq)$$

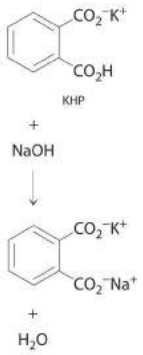
A small amount of soluble starch is added as an indicator. Because starch reacts with excess $I_2$ to give an intense blue color, the appearance of a blue color indicates that the equivalence point of the reaction has been reached.

Adding small volumes of a 0.0031 M aqueous solution of $I_2$ to 194 mL of a solution that contains glutathione and a trace of soluble starch initially causes no change. After 16.3 mL of iodine solution have been added, however, a permanent pale blue color appears because of the formation of the starch-iodine complex. What is the concentration of glutathione in the original solution?

**Answer**

$5.2 \times 10^{-4}$ M

## Standard Solutions




**The reaction of KHP with NaOH.** As with all acid-base reactions, a salt is formed.

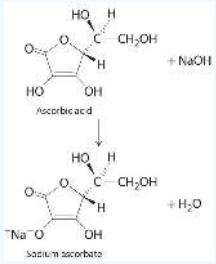
In Example 4.9.1, the concentration of the titrant was accurately known. The accuracy of any titration analysis depends on an accurate knowledge of the concentration of the titrant. Most titrants are first *standardized*; that is, their concentration is measured by titration with a standard solutionA solution whose concentration is precisely known., which is a solution whose concentration is known precisely. Only pure crystalline compounds that do not react with water or carbon dioxide are suitable for use in preparing a standard solution. One such compound is potassium hydrogen phthalate (KHP), a weak monoprotic acid suitable for standardizing solutions of bases such as sodium hydroxide. The reaction of KHP with NaOH is a simple acid–base reaction. If the concentration of the KHP solution is known accurately and the titration of a NaOH solution with the KHP solution is carried out carefully, then the concentration of the NaOH solution can be calculated precisely. The standardized NaOH solution can then be used to titrate a solution of an acid whose concentration is unknown.

## Acid–Base Titrations

Because most common acids and bases are not intensely colored, a small amount of an acid–base **indicator** is usually added to detect the equivalence point in an acid–base titration. The point in the titration at which an indicator changes color is called the endpointThe point in a titration at which an indicator changes color.. The procedure is illustrated in Example 21.

### Example 4.9.2

The structure of vitamin C (ascorbic acid, a monoprotic acid) is as follows:




**Ascorbic acid.** The upper figure shows the three-dimensional representation of ascorbic acid. Hatched lines indicate bonds that are behind the plane of the paper, and wedged lines indicate bonds that are out of the plane of the paper.

An absence of vitamin C in the diet leads to the disease known as scurvy, a breakdown of connective tissue throughout the body and of dentin in the teeth. Because fresh fruits and vegetables rich in vitamin C are readily available in developed countries today, scurvy is not a major problem. In the days of slow voyages in wooden ships, however, scurvy was common. Ferdinand Magellan, the first person to sail around the world, lost more than 90% of his crew, many to scurvy. Although a diet rich in fruits and vegetables contains more than enough vitamin C to prevent scurvy, many people take supplemental doses of vitamin C, hoping that the extra amounts will help prevent colds and other illness.

Suppose a tablet advertised as containing 500 mg of vitamin C is dissolved in 100.0 mL of distilled water that contains a small amount of the acid–base indicator bromothymol blue, an indicator that is yellow in acid solution and blue in basic solution, to give a yellow solution. The addition of 53.5 mL of a 0.0520 M solution of NaOH results in a change to green at the endpoint, due to a mixture of the blue and yellow forms of the indicator What is the actual mass of vitamin C in the tablet? (The molar mass of ascorbic acid is 176.13 g/mol.)

*The solution, containing bromothymol blue as an indicator, is initially yellow (a). The addition of a trace excess of NaOH causes the solution to turn green at the endpoint (b) and then blue.*

**Given:** reactant, volume of sample solution, and volume and molarity of titrant

**Asked for:** mass of unknown

**Strategy:**

**A** Write the balanced chemical equation for the reaction and calculate the number of moles of base needed to neutralize the ascorbic acid.

**B** Using mole ratios, determine the amount of ascorbic acid consumed. Calculate the mass of vitamin C by multiplying the number of moles of ascorbic acid by its molar mass.

**Solution**

**A** Because ascorbic acid acts as a monoprotic acid, we can write the balanced chemical equation for the reaction as

$$HAsc(aq) + OH^-(aq) \rightarrow Asc^-(aq) + H_2O(l)$$

where HAsc is ascorbic acid and $Asc^-$ is ascorbate. The number of moles of $OH^-$ ions needed to neutralize the ascorbic acid is

$$moles\ OH^- = 53.5\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.0520\ mol\ OH^-}{1\ \cancel{L}}\right) = 2.78 \times 10^{-3}\ mol\ OH^-$$

**B** The mole ratio of the base added to the acid consumed is 1:1, so the number of moles of $OH^-$ added equals the number of moles of ascorbic acid present in the tablet:

$$mass\ ascorbic\ acid = 2.78 \times 10^{-3}\ \cancel{mol\ HAsc}\left(\frac{176.13\ g\ HAsc}{1\ \cancel{mol\ HAsc}}\right) = 0.490\ g\ HAsc$$

Because 0.490 g equals 490 mg, the tablet contains about 2% less vitamin C than advertised.

**? Exercise 4.9.2**

Vinegar is essentially a dilute solution of acetic acid in water. Vinegar is usually produced in a concentrated form and then diluted with water to give a final concentration of 4%–7% acetic acid; that is, a 4% m/v solution contains 4.00 g of acetic acid per 100 mL of solution. If a drop of bromothymol blue indicator is added to 50.0 mL of concentrated vinegar stock and 31.0 mL of 2.51 M NaOH are needed to turn the solution from yellow to green, what is the percentage of acetic acid in the vinegar stock? (Assume that the density of the vinegar solution is 1.00 g/mL.)

**Answer**

9.35%

## Summary

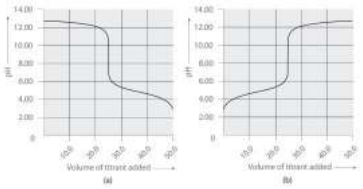
The concentration of a species in solution can be determined by **quantitative analysis**. One such method is a **titration**, in which a measured volume of a solution of one substance, the **titrant**, is added to a solution of another substance to determine its concentration. The **equivalence point** in a titration is the point at which exactly enough reactant has been added for the reaction to go to completion. A **standard solution**, a solution whose concentration is known precisely, is used to determine the concentration of the titrant. Many titrations, especially those that involve acid–base reactions, rely on an indicator. The point at which a color change is observed is the **endpoint**, which is close to the equivalence point if the indicator is chosen properly.

### Key Takeaway

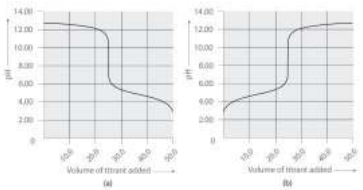
- Quantitative analysis of an unknown solution can be achieved using titration methods.

### Conceptual Problems

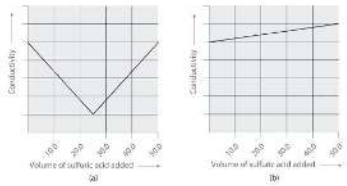
1. The titration procedure is an application of the use of limiting reactants. Explain why this is so.
2. Explain how to determine the concentration of a substance using a titration.
3. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M acetic acid with 0.10 M NaOH, and the other corresponds to the titration of 100 mL 0.10 M NaOH with 0.10 M acetic acid. Which graph corresponds to which titration? Justify your answer.



4. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M ammonia with 0.10 M HCl, and the other corresponds to the titration of 100 mL 0.10 M $NH_4Cl$ with 0.10 M NaOH. Which graph corresponds to which titration? Justify your answer.



5. Following are two graphs that illustrate how the electrical conductivity of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M $Ba(OH)_2$ with 0.10 M $H_2SO_4$ , and the other corresponds to the titration of 100 mL of 0.10 M NaOH with 0.10 M $H_2SO_4$. Which graph corresponds to which titration? Justify your answer.



## Answers

1.
2.
3. 1. titration of NaOH with acetic acid
   2. titration of acetic acid with NaOH
4.
5. 1. titration of $Ba(OH)_2$ with sulfuric acid
   2. titration of NaOH with sulfuric acid

## Numerical Problems

1. A 10.00 mL sample of a 1.07 M solution of potassium hydrogen phthalate (KHP, formula mass = 204.22 g/mol) is diluted to 250.0 mL. What is the molarity of the final solution? How many grams of KHP are in the 10.00 mL sample?
2. What volume of a 0.978 M solution of NaOH must be added to 25.0 mL of 0.583 M HCl to completely neutralize the acid? How many moles of NaOH are needed for the neutralization?
3. A student was titrating 25.00 mL of a basic solution with an HCl solution that was 0.281 M. The student ran out of the HCl solution after having added 32.46 mL, so she borrowed an HCl solution that was labeled as 0.317 M. An additional 11.5 mL of the second solution was needed to complete the titration. What was the concentration of the basic solution?

## Contributors

- Anonymous

Modified by Joshua Halpern (Howard University)

Video 8.9.1 from chemistrynakajima @ YouTube

Video 8.9.2 from MrAmit448 @ YouTube

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# 4.10: Oxidation-Reduction Reactions

**Learning Objectives**

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions in Chapter 3. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method. We show you how to balance redox equations using oxidation states in this section; the half-reaction method is discussed in the second semester

## Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state methodA procedure for balancing oxidation–reduction (redox) reactions in which the overall reaction is conceptually separated into two parts: an oxidation and a reduction., we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of $Cr^{2+}$(aq) with manganese dioxide ($MnO_2$) in the presence of dilute acid. Equation 4.9.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described in Section 3.5:

$$\overset{+2}{Cr^{2+}}(aq) + \overset{+4\ \ -2}{MnO_2}(aq) + \overset{+1}{H^+}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq) + \overset{+2}{Mn^{2+}}(aq) + \overset{+1\ \ -2}{H_2O}(l) \tag{4.10.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced:

$$Cr^{2+} + Mn^{4+} \rightarrow Cr^{3+} + Mn^{2+} \tag{4.10.2}$$

The oxidation can be written as

$$Cr^{2+} \rightarrow Cr^{3+} + e^- \tag{4.10.3}$$

and the reduction as

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+} \tag{4.10.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation equation by 2 to give

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^- \tag{4.10.5}$$

### Note the Pattern

In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction:

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^- \tag{4.10.6}$$

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+} \tag{4.10.7}$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2Cr^{2+}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + \cancel{2e^-}$$

$$\cancel{2e^-} + 2Cr^{2+}\,(aq) \rightarrow Mn^{2+}\,(aq) \tag{4.10.8}$$

$$2Cr^{2+}\,(aq) + 2Cr^{2+}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + Mn^{2+}\,(aq)$$

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of the equation (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add $H^+$ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding $OH^-$ as necessary to either side of the equation to balance the charges. In this case, adding four $H^+$ ions to the left side of the equation gives

$$2Cr^{2+}(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq) \tag{4.10.9}$$

Although the charges are now balanced, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding $H_2O$ as necessary to either side of the equation. Here, we need to add two $H_2O$ molecules to the right side:

$$2Cr^{2+}(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq) + 2H_2O(l) \tag{4.10.10}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized in Table 4.10.1 and illustrated in Example 17.

Table 4.10.1 Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding $H^+$ or $OH^-$ ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding $H_2O$ molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

## Example 4.10.1

Arsenic acid ($H_3AsO_4$) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine ($AsH_3$, a highly toxic and unstable gas) and $Zn^{2+}$(aq). Balance the equation for this reaction using oxidation states:

$$H_3AsO_4(aq) + Zn(s) \rightarrow AsH_3(g) + Zn^{2+}(aq)$$

**Given:** reactants and products in acidic solution

**Asked for:** balanced chemical equation using oxidation states

**Strategy:**

Follow the procedure given in Table 4.10.1 for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

**Solution**

1. **Write a chemical equation showing the reactants and the products.** Because we are given this information, we can skip this step.

2. **Assign oxidation states using the procedure described in Section 4.9 and determine which atoms change oxidation state.** The oxidation state of arsenic in arsenic acid is +6, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$[\mathrm{H_3\overset{+5}{As}\,O_4(aq) + \overset{0}{Zn}\,(s) \rightarrow \underset{-3}{As}\,H_3(g) + \overset{+2}{Zn^{2+}}\,(aq)}]$$

3. **Write separate equations for oxidation and reduction.** The arsenic atom in $H_3AsO_4$ is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$Reduction\text{: } As^{5+} + 8e^- \rightarrow \underset{-3}{As^{3-}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$Oxidation\text{: } Zn \rightarrow Zn^{2+} + 2e^-$$

4. **Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.** The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\begin{aligned} &Reduction\ (\times 1)\text{: } As^{5+} + 8e^- \rightarrow As^{3-} \\ &Oxidation\ (\times 4)\text{: } 4Zn^0 \rightarrow 4Zn^{2+} + 8e^- \end{aligned} \tag{4.10.11}$$

5. **Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.** Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives

$$\begin{aligned} &Reduction\text{: } H_3AsO_4(aq) + 8e^- \rightarrow AsH_3(g) \\ &Oxidation\text{: } 4Zn(s) \rightarrow 4Zn^{2+}(aq) + 8e^- \end{aligned} \tag{4.10.12}$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is $H_3AsO_4(aq) + 4Zn(s) + \cancel{8e^-} \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + \cancel{8e^-}$

   which then yields

   $$H_3AsO_4(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4Zn^{2+}(aq)$$

7. *Balance the charge by adding $H^+$ or $OH^-$ ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add $H^+$ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight $H^+$ ions to the left side gives a charge of +8 on both sides of the equation: $H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq)$

8. *Balance the oxygen atoms by adding $H_2O$ molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 $H_2O$ molecules to the right side balances the O atoms: $H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$

   Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:

$$\begin{aligned} &Atoms\text{: } 1As + 4Zn + 4O + 11H = 1As + 4Zn + 4O + 11H \\ &Total\ charge\text{: } 8(+1) = 4(+2) = +8 \end{aligned} \tag{4.10.13}$$

The balanced chemical equation for the reaction is therefore:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

## ? Exercise 4.10.1

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$CuS(s) + H^+(aq) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO(g) + SO_4^{2-}(aq)$$

**Answer**

$3CuS(s) + 8H^+(aq) + 8NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 8NO(g) + 3SO_4^{2-}(aq) + 4H_2O(l)$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 18.

## Example 4.10.2

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$Al(s) + H_2O(aq) \rightarrow [Al(OH)_4]^-(aq) + H_2(g)$$

Balance this equation using oxidation states.

**Given:** reactants and products in a basic solution

**Asked for:** balanced chemical equation

**Strategy:**

Follow the procedure given in Table 4.10.1 for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

**Solution**

We will apply the same procedure used in Example 17 but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[Al(OH)_4]^-$. The oxidation state of hydrogen changes from +1 in $H_2O$ to 0 in $H_2$. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}(s) + \overset{+1}{H}_2O(aq) \rightarrow [\overset{+3}{Al}(OH)_4]^-(aq) + \overset{0}{H}_2(g)$$

3. $Reduction: Al^0 \rightarrow Al^{3+} + 3e^-$ (4.10.14)
   $Oxidation: H^+ + e^- \rightarrow H^0\ (in\ H_2)$ (4.10.15)
4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
   $Reduction: 3H^+ + 3e^- \rightarrow 3H^0\ (in\ H_2)$ (4.10.16)
   $Oxidation: Al^0 \rightarrow Al^{3+} + 3e^-$ (4.10.17)
5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of $H_2O$ contains two protons, in this case, $3H^+$ corresponds to $3/2H_2O$. Similarly, each molecule of hydrogen gas contains two H atoms, so 3H corresponds to $3/2H_2$.

   $Reduction: \frac{3}{2}H_2O + 3e^- \rightarrow \frac{3}{2}H_2$ (4.10.18)
   $Oxidation: Al \rightarrow [Al(OH)_4]^- + 3e^-$ (4.10.19)
6. Adding the equations and canceling the electrons gives $Al + \frac{3}{2}H_2O + \cancel{3e^-} \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2 + \cancel{3e^-}$
   $Al + \frac{3}{2}H_2O \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

   $2Al + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$
7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two $OH^-$ ions to the left side: $2Al + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$
8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three $H_2O$ molecules to the left side: $2Al + 2OH^- + 6H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$

9. Be sure the equation is balanced:
   $Atoms: 2Al + 8O + 14H = 2Al + 8O + 14H$ (4.10.20)
   $Total\ charge: (2)(0) + (2)(-1) + (6)(0) = (2)(-1) + (3)(0)$ (4.10.21)
   $-2 = -2$
10. The balanced chemical equation is therefore $2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$

    Thus 3 mol of $H_2$ gas are produced for every 2 mol of Al.

**? Exercise 4.10.2**

The permanganate ion reacts with nitrite ion in basic solution to produce manganese(IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

**Answer**

$2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$

As suggested in Example 17 and Example 18, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

Compounds of elements in high oxidation states (such as $ClO_4^-$, $NO_3^-$, $MnO_4^-$, $Cr_2O_7^{2-}$, and $UF_6$) tend to act as *oxidants* and *become reduced* in chemical reactions. Compounds of elements in low oxidation states (such as $CH_4$, $NH_3$, $H_2S$, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

### Note the Pattern

Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

## Redox Reactions of Solid Metals in Aqueous Solution

A widely encountered class of oxidation–reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure 4.10.1 ). Rust is formed from a complex oxidation–reduction reaction involving dilute acid solutions that contain $Cl^-$ ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with HCl(aq) to produce iron(II) chloride and hydrogen gas:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \quad (4.10.22)$$

In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.

Figure 4.10.1 Rust Formation



*The corrosion process involves an oxidation–reduction reaction in which metallic iron is converted to $Fe(OH)_3$, a reddish-brown solid.*

Many metals dissolve through reactions of this type, which have the general form

$$metal + acid \rightarrow salt + hydrogen \tag{4.10.23}$$

Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids. In the presence of these acids, lead dissolves:

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g) \tag{4.10.24}$$

Consequently, it has been speculated that both the water and the food consumed by Romans contained toxic levels of lead, which resulted in widespread lead poisoning and eventual madness. Perhaps this explains why the Roman Emperor Caligula appointed his favorite horse as consul!

## Single-Displacement Reactions

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 4.10.13 ) and the reduction of silver salts by copper (Equation 4.10.14 and Figure 4.10.2 ):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s) \tag{4.10.25}$$

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

The reaction in Equation 4.10.13 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.

Figure 4.10.2 The Single-Displacement Reaction of Metallic Copper with a Solution of Silver Nitrate



Figure used with permission of Wikipedia

## The Activity Series

By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, we saw in Equation 8.10.13 and Equation 8.10.14 that metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing $Zn^{2+}$. Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:

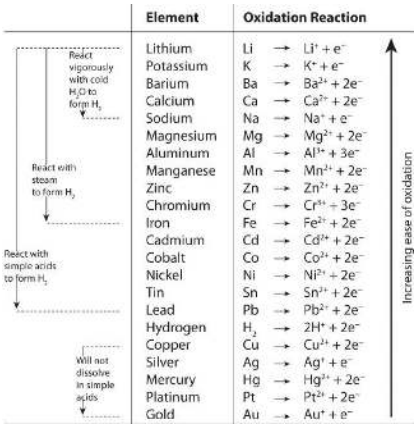
$$Zn(s) + Mg^{2+}(aq) \not\rightarrow Zn^{2+}(aq) + Mg(s) \tag{4.10.26}$$

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s) \tag{4.10.27}$$

Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure 4.10.3 ), which lists metals and hydrogen in order of their relative tendency to be oxidized. The metals at the top of the series, which have the greatest tendency to lose electrons, are the alkali metals (group 1), the alkaline earth metals (group 2), and Al (group 13). In contrast, the metals at the bottom of the series, which have the lowest tendency to be oxidized, are the precious metals or coinage metals—platinum, gold, silver, and copper, and mercury, which are located in the lower right portion of the metals in the periodic table. You should be generally familiar with which kinds of metals are active metals The metals at the top of the activity series, which have the greatest tendency to be oxidized. (located at the top of the series) and which are inert metals The metals at the bottom of the activity series, which have the least tendency to be oxidized. (at the bottom of the series).

Figure 4.10.3 The Activity Series




When using the activity series to predict the outcome of a reaction, keep in mind that *any element will reduce compounds of the elements below it in the series*. Because magnesium is above zinc in Figure 4.10.3, magnesium metal will reduce zinc salts but not vice versa. Similarly, the precious metals are at the bottom of the activity series, so virtually any other metal will reduce precious metal salts to the pure precious metals. Hydrogen is included in the series, and the tendency of a metal to react with an acid is

indicated by its position relative to hydrogen in the activity series. *Only those metals that lie above hydrogen in the activity series dissolve in acids to produce $H_2$.* Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore do not corrode readily. Example 19 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions. We will return to the activity series when we discuss oxidation–reduction reactions in more detail in Chapter 19 .

### Example 4.10.3

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

1. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
2. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
3. Some sulfuric acid from a car battery is accidentally spilled on the lead cable terminals.

**Given:** reactants

**Asked for:** overall reaction and net ionic equation

**Strategy:**

**A** Locate the reactants in the activity series in Figure 4.10.3 and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.

**B** Write the net ionic equation for the redox reaction.

**Solution**

1. **A** Aluminum is an active metal that lies above silver in the activity series, so we expect a reaction to occur. According to their relative positions, aluminum will be oxidized and dissolve, and silver ions will be reduced to silver metal. **B** The net ionic equation is as follows:

   $$Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$$

   Recall from our discussion of solubilities that most nitrate salts are soluble. In this case, the nitrate ions are spectator ions and are not involved in the reaction.

2. **A** Mercury lies below lead in the activity series, so no reaction will occur.
3. **A** Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form $H_2$. **B** From our discussion of solubilities, recall that $Pb^{2+}$ and $SO_4^{2-}$ form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:

   $$Pb(s) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + H_2(g)$$

   Lead(II) sulfate is the white solid that forms on corroded battery terminals.



**Corroded battery terminals.** The white solid is lead(II) sulfate, formed from the reaction of solid lead with a solution of sulfuric acid.

**? Exercise 4.10.3**

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

1. A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
2. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
3. A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

**Answer**

1. *no reaction*
2. $3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$
3. $2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^-(aq) + 3H_2(g)$

## Summary

In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the **oxidation state method** (Table 8.9.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 4.10.3, which arranges metals and $H_2$ in decreasing order of their tendency to be oxidized. Any metal will reduce metal ions below it in the activity series. **Active metals** lie at the top of the activity series, whereas **inert metals** are at the bottom of the activity series.

## Key Takeaway

- Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation.

## Conceptual Problems

1. Which elements in the periodic table tend to be good oxidants? Which tend to be good reductants?
2. If two compounds are mixed, one containing an element that is a poor oxidant and one with an element that is a poor reductant, do you expect a redox reaction to occur? Explain your answer. What do you predict if one is a strong oxidant and the other is a weak reductant? Why?
3. In each redox reaction, determine which species is oxidized and which is reduced:
   a. $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$
   b. $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$
   c. $BrO_3^-(aq) + 2MnO_2(s) + H_2O(l) \rightarrow Br^-(aq) + 2MnO_4^-(aq) + 2H^+(aq)$
4. Single-displacement reactions are a subset of redox reactions. In this subset, what is oxidized and what is reduced? Give an example of a redox reaction that is *not* a single-displacement reaction.
5. Of the following elements, which would you expect to have the greatest tendency to be oxidized: Zn, Li, or S? Explain your reasoning.
6. Of these elements, which would you expect to be easiest to reduce: Se, Sr, or Ni? Explain your reasoning.
7. Which of these metals produces $H_2$ in acidic solution?
   a. Ag
   b. Cd
   c. Ca
   d. Cu
8. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.
   a. $Mg(s) + Cu^{2+}(aq) \rightarrow$

b. $Au(s) + Ag^{+}(aq) \rightarrow$
c. $Cr(s) + Pb^{2+}(aq) \rightarrow$
d. $K(s) + H_2O(l) \rightarrow$
e. $Hg(l) + Pb^{2+}(aq) \rightarrow$

## Numerical Problems

1. Balance each redox reaction under the conditions indicated.

   a. $CuS(s) + NO_3^{-}(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + NO(g)$; acidic solution
   b. $Ag(s) + HS^{-}(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2S(s) + Cr(OH)_3(s)$; basic solution
   c. $Zn(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + H_2(g)$; acidic solution
   d. $O_2(g) + Sb(s) \rightarrow H_2O_2(aq) + SbO_2^{-}(aq)$; basic solution
   e. $UO_2^{2+}(aq) + Te(s) \rightarrow U^{4+}(aq) + TeO_4^{2-}(aq)$; acidic solution

2. Balance each redox reaction under the conditions indicated.

   a. $MnO_4^{-}(aq) + S_2O_3^{2-}(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$; acidic solution
   b. $Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$; acidic solution
   c. $Fe(s) + CrO_4^{2-}(aq) \rightarrow Fe_2O_3(s) + Cr_2O_3(s)$; basic solution
   d. $Cl_2(aq) \rightarrow ClO_3^{-}(aq) + Cl^{-}(aq)$; acidic solution
   e. $CO_3^{2-}(aq) + N_2H_4(aq) \rightarrow CO(g) + N_2(g)$; basic solution

3. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.

   a. Platinum wire is dipped in hydrochloric acid.
   b. Manganese metal is added to a solution of iron(II) chloride.
   c. Tin is heated with steam.
   d. Hydrogen gas is bubbled through a solution of lead(II) nitrate.

4. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.

   a. A few drops of $NiBr_2$ are dropped onto a piece of iron.
   b. A strip of zinc is placed into a solution of HCl.
   c. Copper is dipped into a solution of $ZnCl_2$.
   d. A solution of silver nitrate is dropped onto an aluminum plate.

5. Dentists occasionally use metallic mixtures called *amalgams* for fillings. If an amalgam contains zinc, however, water can contaminate the amalgam as it is being manipulated, producing hydrogen gas under basic conditions. As the filling hardens, the gas can be released, causing pain and cracking the tooth. Write a balanced chemical equation for this reaction.

6. Copper metal readily dissolves in dilute aqueous nitric acid to form blue $Cu^{2+}(aq)$ and nitric oxide gas.

   a. What has been oxidized? What has been reduced?
   b. Balance the chemical equation.

7. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:

   a. $Pt^{2+}(aq) + Ag(s) \rightarrow$
   b. $HCN(aq) + NaOH(aq) \rightarrow$
   c. $Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow$
   d. $CH_4(g) + O_2(g) \rightarrow$

8. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:

   a. $Zn(s) + HCl(aq) \rightarrow$

b. $HNO_3(aq) + AlCl_3(aq) \rightarrow$
c. $K_2CrO_4(aq) + Ba(NO_3)_2(aq) \rightarrow$
d. $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$

## Contributors

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# 4.11: Essential Skills 3

**Learning Objectives**

- Base-10 Logarithms
- Calculations Using Common Logarithm

Essential Skills 1 and Essential Skills 2 described some fundamental mathematical operations used for solving problems in chemistry. This section introduces you to base-10 logarithms, a topic with which you must be familiar to do the Questions and Problems for end of Chapter 4.

## Base-10 (Common) Logarithms

Essential Skills 1 introduced exponential notation, in which a base number is multiplied by itself the number of times indicated in the exponent. The number $10^3$, for example, is the base 10 multiplied by itself three times (10 × 10 × 10 = 1000). Now suppose that we do not know what the exponent is—that we are given only a base of 10 and the final number. If our answer is 1000, the problem can be expressed as

$$10^a = 1000$$

We can determine the value of *a* by using an operation called the *base-10 logarithm*, or *common logarithm*, abbreviated as *log*, that represents the power to which 10 is raised to give the number to the right of the equals sign. This relationship is stated as $\log 10^a = a$. In this case, the logarithm is 3 because $10^3 = 1000$:

$$log\, 10^3 = 3$$

$$log\, 1000 = 3$$

Now suppose you are asked to find *a* when the final number is 659. The problem can be solved as follows (remember that any operation applied to one side of an equality must also be applied to the other side):

$$10^a = 659$$

$$log\, 10^a = log\, 659$$

$$a = log\, 659$$

If you enter 659 into your calculator and press the "log" key, you get 2.819, which means that $a = 2.819$ and $10^{2.819} = 659$. Conversely, if you enter the value 2.819 into your calculator and press the "$10^x$" key, you get 659.

You can decide whether your answer is reasonable by comparing it with the results you get when $a = 2$ and $a = 3$:

$$a = 2\text{: } 10^2 = 100$$

$$a = 2.819\text{: } 10^{2.819} = 659$$

$$a = 3\text{: } 10^3 = 1000$$

Because the number 659 is between 100 and 1000, *a* must be between 2 and 3, which is indeed the case. Table 4.11.1 lists some base-10 logarithms, their numerical values, and their exponential forms.

Table 4.11.1 Relationships in Base-10 Logarithms

| Numerical Value | Exponential Form | Logarithm ($a$) |
|---|---|---|
| 1000 | $10^3$ | 3 |
| 100 | $10^2$ | 2 |
| 10 | $10^1$ | 1 |
| 1 | $10^0$ | 0 |
| 0.1 | $10^{-1}$ | −1 |
| 0.01 | $10^{-2}$ | −2 |
| 0.001 | $10^{-3}$ | −3 |

Base-10 logarithms may also be expressed as $\log_{10}$, in which the base is indicated as a subscript. We can write $\log 10^a = a$ in either of two ways:

$$log\ 10^a = a$$

$$log_{10} = (10^a) = a$$

The second equation explicitly indicates that we are solving for the base-10 logarithm of $10^a$.

The number of significant figures in a logarithmic value is the same as the number of digits *after* the decimal point in its logarithm, so log 62.2, a number with three significant figures, is 1.794, with three significant figures after the decimal point; that is, $10^{1.794}$ = 62.2, *not* 62.23. Skill Builder ES1 provides practice converting a value to its exponential form and then calculating its logarithm.

### Skill Builder ES1

Express each number as a power of 10 and then find the common logarithm.

1. 10,000
2. 0.00001
3. 10.01
4. 2.87
5. 0.134

Solution

1. 10,000 = $1 \times 10^4$; $\log 1 \times 10^4 = 4.0$
2. 0.00001 = $1 \times 10^{-5}$; $\log 1 \times 10^{-5} = -5.0$
3. 10.01 = $1.001 \times 10$; log 10.01 = 1.0004 (enter 10.01 into your calculator and press the “log” key); $10^{1.0004} = 10.01$
4. 2.87 = $2.87 \times 10^0$; log 2.87 = 0.458 (enter 2.87 into your calculator and press the “log” key); $10^{0.458} = 2.87$
5. 0.134 = $1.34 \times 10^{-1}$; log 0.134 = −0.873 (enter 0.134 into your calculator and press the “log” key); $10^{-0.873} = 0.134$

### Skill Builder ES2

Convert each base-10 logarithm to its numerical value.

1. 3
2. −2.0
3. 1.62
4. −0.23
5. −4.872

Solution

1. $10^3$
2. $10^{-2}$
3. $10^{1.62} = 42$

4. $10^{-0.23} = 0.59$
5. $10^{-4.872} = 1.34 \times 10^{-5}$

## Calculations Using Common Logarithms

Because logarithms are exponents, the properties of exponents that you learned in Essential Skills 1 apply to logarithms as well, which are summarized in Table 4.11.1. The logarithm of (4.08 × 20.67), for example, can be computed as follows:

$$log(4.08 \times 20.67) = log\, 4.08 + log\, 20.67 = 0.611 + 1.3153 = 1.926$$

We can be sure that this answer is correct by checking that $10^{1.926}$ is equal to 4.08 × 20.67, and it is.

In an alternative approach, we multiply the two values before computing the logarithm:

$$4.08 \times 20.67 = 84.3$$

$$log\, 84.3 = 1.926$$

We could also have expressed 84.3 as a power of 10 and then calculated the logarithm:

$$log\, 84.3 = log(8.43 \times 10) = log\, 8.43 + log\, 10 = 0.926 + 1 = 1.926$$

As you can see, *there may be more than one way to correctly solve a problem*.

We can use the properties of exponentials and logarithms to show that the logarithm of the inverse of a number (1/*B*) is the negative logarithm of that number (−log *B*):

$$log\left(\tfrac{1}{B}\right) = -log\,(B)$$

If we use the formula for division given Table 8.6 and recognize that log 1 = 0, then the logarithm of 1/*B* is

$$log\left(\tfrac{1}{B}\right) = log\,(1) - log\,(B) = -log\,(B)$$

**Table 8.11.2 Properties of Logarithms**

| Operation | Exponential Form | Logarithm |
|---|---|---|
| multiplication | $(10^a)(10^b) = 10^{a+b}$ | $log(ab) = log\, a + log\, b$ |
| division | $\frac{10^a}{10^b} = 10^{a-b}$ | $log\left(\frac{a}{b}\right) = log\, a - log\, b$ |

### Skill Builder ES3

Convert each number to exponential form and then calculate the logarithm (assume all trailing zeros on whole numbers are not significant).

1. 100 × 1000
2. 0.100 ÷ 100
3. 1000 × 0.010
4. 200 × 3000
5. 20.5 ÷ 0.026

Solution

1. 100 × 1000 = $(1 \times 10^2)(1 \times 10^3)$

   $\log[(1 \times 10^2)(1 \times 10^3)] = 2.0 + 3.0 = 5.0$

   Alternatively, $(1 \times 10^2)(1 \times 10^3) = 1 \times 10^{2+3} = 1 \times 10^5$

   $\log(1 \times 10^5) = 5.0$

2. 0.100 ÷ 100 = $(1.00 \times 10^{-1}) \div (1 \times 10^2)$

   $\log[(1.00 \times 10^{-1}) \div (1 \times 10^2)] = 1 \times 10^{-1-2} = 1 \times 10^{-3}$

   Alternatively, $(1.00 \times 10^{-1}) \div (1 \times 10^2) = 1 \times 10^{[(-1)-2]} = 1 \times 10^{-3}$

$\log(1 \times 10^{-3}) = -3.0$

3. $1000 \times 0.010 = (1 \times 10^3)(1.0 \times 10^{-2})$

   $\log[(1 \times 10^3)(1 \times 10^{-2})] = 3.0 + (-2.0) = 1.0$

   Alternatively, $(1 \times 10^3)(1.0 \times 10^{-2}) = 1 \times 10^{[3 + (-2)]} = 1 \times 10^1$

   $\log(1 \times 10^1) = 1.0$

4. $200 \times 3000 = (2 \times 10^2)(3 \times 10^3)$

   $\log[(2 \times 10^2)(3 \times 10^3)] = \log(2 \times 10^2) + \log(3 \times 10^3)$

   $= (\log 2 + \log 10^2) + (\log 3 + \log 10^3)$

   $= 0.30 + 2 + 0.48 + 3 = 5.8$

   Alternatively, $(2 \times 10^2)(3 \times 10^3) = 6 \times 10^{2 + 3} = 6 \times 10^5$

   $\log(6 \times 10^5) = \log 6 + \log 10^5 = 0.78 + 5 = 5.8$

5. $20.5 \div 0.026 = (2.05 \times 10) \div (2.6 \times 10^{-2})$

   $\log[(2.05 \times 10) \div (2.6 \times 10^{-2})] = (\log 2.05 + \log 10) - (\log 2.6 + \log 10^{-2})$

   $= (0.3118 + 1) - [0.415 + (-2)]$

   $= 1.3118 + 1.585 = 2.90$

   Alternatively, $(2.05 \times 10) \div (2.6 \times 10^{-2}) = 0.788 \times 10^{[1 - (-2)]} = 0.788 \times 10^3$

   $\log(0.79 \times 10^3) = \log 0.79 + \log 10^3 = -0.102 + 3 = 2.90$

## Skill Builder ES4

Convert each number to exponential form and then calculate its logarithm (assume all trailing zeros on whole numbers are not significant).

1. $10 \times 100{,}000$
2. $1000 \div 0.10$
3. $25{,}000 \times 150$
4. $658 \div 17$

Solution

1. $(1 \times 10)(1 \times 10^5)$; logarithm = 6.0
2. $(1 \times 10^3) \div (1.0 \times 10^{-1})$; logarithm = 4.00
3. $(2.5 \times 10^4)(1.50 \times 10^2)$; logarithm = 6.57
4. $(6.58 \times 10^2) \div (1.7 \times 10)$; logarithm = 1.59

## Contributors

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# CHAPTER OVERVIEW

## 5: Energy Changes in Chemical Reactions


5.1: Energy Changes in Chemical Reactions
5.2: Enthalpy and Reactions
5.3: Hess's Law
5.4: Heats of Formation
5.5: Enthalpies of Solution
5.6: Calorimetry
5.7: Thermochemistry and Nutrition
5.8: Energy Sources and the Environment
5.9: Essential Skills 4


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# 5.1: Energy Changes in Chemical Reactions

**Learning Objectives**

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

## Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 5.1.1 ). Thermal energyEnergy that results from atomic and molecular motion; the faster the motion, the higher the thermal energy. results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperatureA measure of an object's thermal energy content. of an object is a measure of its thermal energy content. Radiant energyOne of the five forms of energy, radiant energy is carried by light, microwaves, and radio waves (the other forms of energy are thermal, chemical, nuclear, and electrical). Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energyOne of the five forms of energy, electrical energy results from the flow of electrically charged particles. The other four forms of energy are radiant, thermal, chemical, and nuclear. results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energyOne of the five forms of energy, nuclear energy is stored in the nucleus of an atom. The other four forms of energy are radiant, thermal, chemical, and electrical. is stored in the nucleus of an atom, and chemical energyOne of the five forms of energy, chemical energy is stored within a chemical compound because of a particular arrangement of atoms. The other four forms of energy are radiant, thermal, nuclear, and electrical. is stored within a chemical compound because of a particular arrangement of atoms.

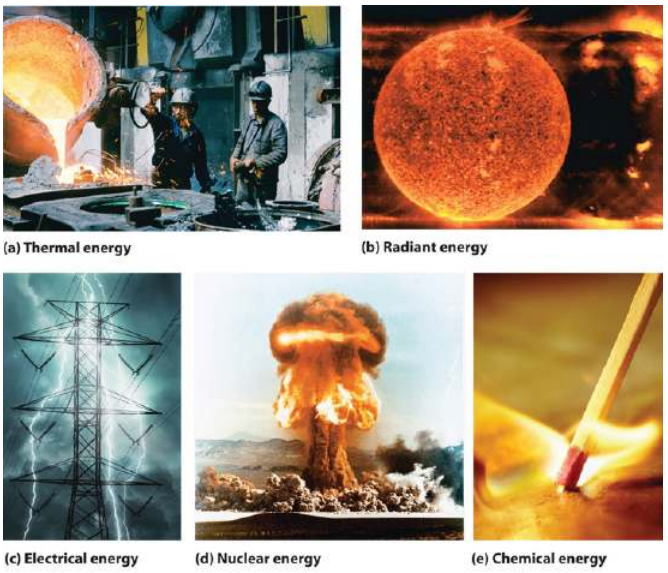



Figure 5.1.1 **Forms of Energy** *(a) Thermal energy results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) Radiant energy (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of electrical energy, which is due to the flow of electrically charged particles. (d) Nuclear energy is released when particles in the nucleus of the atom are rearranged. (e) Chemical energy results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.*

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (*PE*)Energy stored in an object because of its relative position or orientation., which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (*KE*)Energy due to the motion of an object: $1/2\ mv^2$ where $m$ is the mass of the object and $v$ is its velocity. is energy due to the *motion* of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 5.1.2 ) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

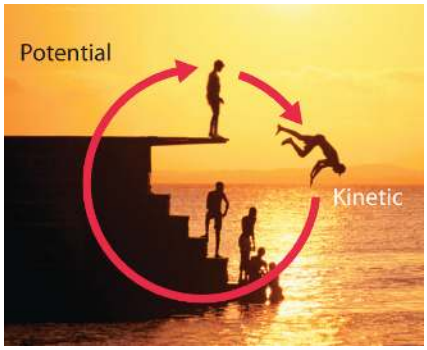



Figure 5.1.2 **Interconversion of Forms of Energy** *When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.*

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the law of conservation of energyThe total amount of energy in the universe remains constant. Energy can be neither created nor destroyed, but it can be converted from one form to another..As you will learn in Chapter 18, the law of conservation of energy is also known as the first law of thermodynamics. *Energy cannot be created or destroyed.*

## Energy, Heat, and Work

One definition of energyThe capacity to do work. is the capacity to do work. The easiest form of work to visualize is mechanical workThe energy required to move an object a distance *d* when opposed by a force *F*, (Figure 5.1.3 ), which is the energy required to move an object a distance *d* when opposed by a force *F*, such as gravity:

$$\begin{aligned} work &= force \times distance \\ w &= Fd \end{aligned} \tag{5.1.1}$$

Because the force (*F*) that opposes the action is equal to the mass (*m*) of the object times its acceleration (*a*), we can also write Equation 9.1.1 as follows:Recall from Chapter 1 that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

$$\begin{aligned} work &= mass \times acceleration \times distance \\ w &= mad \end{aligned} \tag{5.1.2}$$

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things: (1) the height of the second floor (the distance

*d*); (2) your mass, which must be raised that distance against the downward acceleration due to gravity; and (3) your path, as you will learn in Section 9.2.

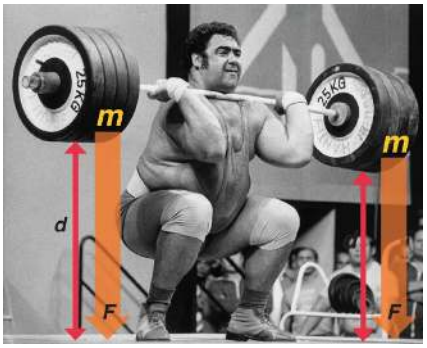



Figure 5.1.3 **An Example of Mechanical Work** *One form of energy is mechanical work, the energy required to move an object of mass m a distance d when opposed by a force F, such as gravity.*

In contrast, heat (*q*)Thermal energy that can be transformed from an object at one temperature to an object at another temperature. is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

The energy of an object can be changed only by the transfer of energy to or from another object in the form of heat, As you learned, hot objects can also lose energy as radiant energy, such as heat or light. This energy is converted to heat when it is absorbed by another object. Hence radiant energy is equivalent to heat. work performed on or by the object, or some combination of heat and work. Consider, for example, the energy stored in a fully charged battery. As shown in Figure 5.1.4, this energy can be used primarily to perform work (e.g., running an electric fan) or to generate light and heat (e.g., illuminating a light bulb). When the battery is fully discharged in either case, the total change in energy is the same, even though the fraction released as work or heat varies greatly. The sum of the heat produced and the work performed equals the change in energy ($\Delta E$):

$$\begin{aligned} EnergyChange(\Delta E) &= work + heat \\ \Delta E &= q + w \end{aligned} \tag{5.1.3}$$

Energy can be transferred only in the form of heat, work performed on or by an object, or some combination of heat and work.

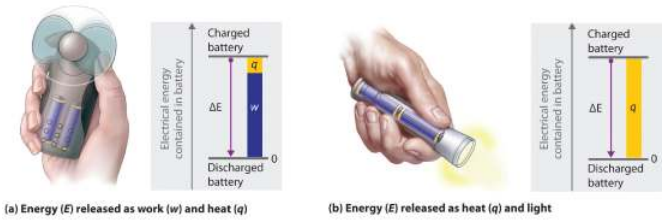



Figure 5.1.4 **Energy Transfer:** *Discharging a fully charged battery releases the same amount of energy whether the battery is used to run a fan (a) or illuminate a light bulb (b). In (a), most of the energy is used to perform work, which turns the blades of the fan and thus moves the air; only a small portion of the energy is released as heat by the electric motor. In (b), all the energy is released as heat and light; no work is done.*

Energy is an extensive property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. (For more information on the properties of matter, see Chapter 1 ) A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

## Kinetic and Potential Energy

The kinetic energy of an object is related to its mass *m* and velocity *v*:

$$KE = \frac{1}{2}mv^2 \tag{5.1.4}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

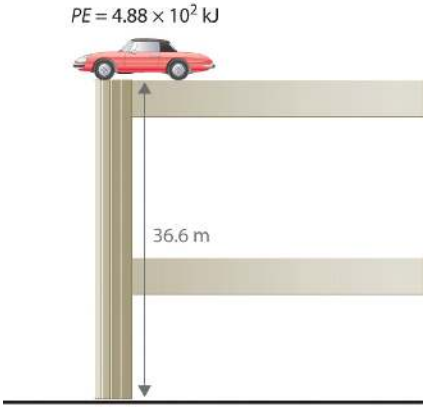
$$KE = \frac{1}{2}mv^2 = \frac{1}{2}\,(1360\ kg) \tag{5.1.5}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J). The joule is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter$^2$/second$^2$ (kg·m$^2$/s$^2$). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = $10^3$ J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × $10^5$ J or 4.88 × $10^2$ kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.

To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is given by Equation 5.1.1 (*w* = *Fd*). According to Equation 5.1.5, the force (*F*) exerted by gravity on any object is equal to its mass (*m*, in this case, 1360 kg) times the acceleration (*a*) due to gravity (*g*, 9.81 m/s$^2$ at Earth's surface). The distance (*d*) is the height (*h*) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

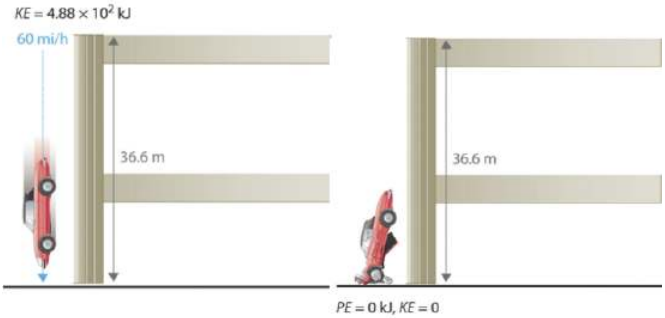
$$\begin{aligned} PE = Fd = mad = mgh \\ PE = (1360\ kg)\,(9.81\ m\ s^{-2})\,(36.6\ m) = 4.88 \times 10^5 kg\ m^2\ s^{-2} \\ = 4.88 \times 10^5 J = 488\ kJ \end{aligned} \tag{5.1.6}$$

The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.




If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.



A recent and spectacular example of the conversion of potential energy to kinetic energy was seen by the earthquake near the east coast of Honshu, Japan, on March 11, 2011. The magnitude 9.0 earthquake occurred along the Japan Trench subduction zone, the interface boundary between the Pacific and North American geological plates. During its westward movement, the Pacific plate became trapped under the North American plate, and its further movement was prevented. When there was sufficient potential energy to allow the Pacific plate to break free, approximately $7.1 \times 10^{15}$ kJ of potential energy was released as kinetic energy, the equivalent of $4.75 \times 10^{8}$ tn of TNT (trinitrotoluene) or 25,003 nuclear bombs. The island of Japan experienced the worst devastation in its history from the earthquake, resulting tsunami, and aftershocks. Historical records indicate that an earthquake of such force occurs in some region of the globe approximately every 1000 years. One such earthquake and resulting tsunami is speculated to have caused the destruction of the lost city of Atlantis, referred to by the ancient Greek philosopher Plato.

### Note the Pattern

The units of energy are the same for all forms of energy.

Energy can also be expressed in the non-SI units of calories (cal)A non-SI unit of energy: 1 cal = 4.184 J exactly., where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$1\ cal = 4.184\ Jexactly$

$1\ J = 0.2390\ cal$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information, addressed in Section 9.7 .

### Example 5.1.1

1. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
2. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

**Given:** mass and velocity or height

**Asked for:** kinetic and potential energy

**Strategy:**

Use Equation 5.1.4 to calculate the kinetic energy and Equation 5.1.6 to calculate the potential energy, as appropriate.

**Solution:**

1. The kinetic energy of an object is given by $1/2\ mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units and then plug the answer into the formulat for kinetic energy
2. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

Exercise

1. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
2. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

**? Exercise 5.1.1**

1. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
2. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

**Answer**

1. $3.10 \times 10^2$ J
2. 65 J

## Key Equations

**general definition of work**

Equation 5.1.1 : $w = Fd$

**relationship between energy, heat, and work**

Equation 5.1.3 : $\Delta E = q + w$

**kinetic energy**

Equation 5.1.4 : $KE = 1/2\ mv^2$

**potential energy in a gravitational field**

Equation 5.1.5.: $PE = mgh$

## Summary

*Thermochemistry* is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed. The most common units of energy are the **joule (J)**, defined as 1 $(kg \cdot m^2)/s^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

## Key Takeaway

- All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

## Conceptual Problems

1. What is the relationship between mechanical work and energy?
2. Does a person with a mass of 50 kg climbing a height of 15 m do work? Explain your answer. Does that same person do work while descending a mountain?
3. If a person exerts a force on an immovable object, does that person do work? Explain your answer.
4. Explain the differences between electrical energy, nuclear energy, and chemical energy.
5. The chapter describes thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy. Which form(s) of energy are represented by each of the following?
    1. sunlight
    2. the energy produced by a cathode ray tube, such as that found in a television
    3. the energy emitted from radioactivity
    4. the energy emitted from a burning candle

5. the energy associated with a steam engine
6. the energy emitted by a cellular phone
7. the energy associated with a stick of dynamite

6. Describe the various forms of energy that are interconverted when a flashlight is switched on.
7. Describe the forms of energy that are interconverted when the space shuttle lifts off.
8. Categorize each of the following as representing kinetic energy or potential energy.
    1. the energy associated with a laptop computer sitting on the edge of a desk
    2. shoveling snow
    3. water pouring out of a fire hydrant
    4. the energy released by an earthquake
    5. the energy in a volcano about to erupt
    6. the energy associated with a coiled spring
9. Are the units for potential energy the same as the units for kinetic energy? Can an absolute value for potential energy be obtained? Explain your answer.
10. Categorize each of the following as representing kinetic energy or potential energy.
    1. water cascading over Niagara Falls
    2. a beaker balanced on the edge of a sink
    3. the energy released during a mudslide
    4. rollerblading
    5. the energy in a block of ice on a rooftop before a thaw
11. Why does hammering a piece of sheet metal cause the metal to heat up?

## Answers

1.
2.
3. Technically, the person is not doing any work, since the object does not move.
4.
5.
6.
7.
8.
9.
10.
11. The kinetic energy of the hammer is transferred to the metal.

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9 )before proceeding to the Numerical Problems.*

1. Describe the mathematical relationship between (a) the thermal energy stored in an object and that object's mass and (b) the thermal energy stored in an object and that object's temperature.
2. How much energy (in kilojoules) is released or stored when each of the following occurs?
    1. A 230 lb football player is lifted to a height of 4.00 ft.
    2. An 11.8 lb cat jumps from a height of 6.50 ft.
    3. A 3.75 lb book falls off of a shelf that is 5.50 ft high.
3. Calculate how much energy (in kilojoules) is released or stored when each of the following occurs:

   1. A 130 lb ice skater is lifted 7.50 ft off the ice.
   2. A 48 lb child jumps from a height of 4.0 ft.
   3. An 18.5 lb light fixture falls from a 10.0 ft ceiling.
4. A car weighing 1438 kg falls off a bridge that is 211 ft high. Ignoring air resistance, how much energy is released when the car hits the water?
5. A 1 tn roller coaster filled with passengers reaches a height of 28 m before accelerating downhill. How much energy is released when the roller coaster reaches the bottom of the hill? Assume no energy is lost due to friction.

## Answers

1. 1. The thermal energy content of an object is directly proportional to its mass.
   2. The thermal energy content of an object is directly proportional to its temperature.
2. 
3. 1. 1.3 kJ stored
   2. 0.26 kJ released
   3. 0.251 kJ released
4. 
5. 250 kJ released

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# 5.2: Enthalpy and Reactions

**Learning Objectives**

- To know the key features of a state function.
- To understand why enthalpy is an important state function.

To study the flow of energy during a chemical reaction, we need to distinguish between a systemThe small, well-defined part of the universe in which we are interested., the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundingsAll the universe that is not the system; that is, system + surroundings = universe., the rest of the universe, including the container in which the reaction is carried out (Figure 5.2.1 ). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

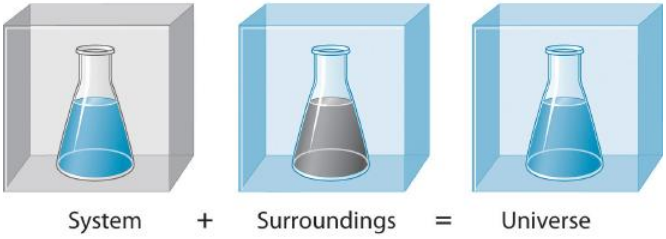



**Figure** 5.2.1 **A System and Its Surroundings** *The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.*

Three kinds of systems are important in chemistry. An open systemA system that can exchange both matter and energy with its surroundings. can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A closed systemA system that can exchange energy but not matter with its surroundings. can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An isolated systemA system that can exchange neither energy nor matter with its suroundings. exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a systemA complete description of the system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state functionA property of a system whose magnitude depends on only the present state of the system, not its previous history. is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 5.2.2 ). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they

simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.




Figure 5.2.2 **Elevation as an Example of a State Function** *The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are not state functions.*

## Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (see chapter opening image). The balanced chemical equation for the reaction is as follows:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) \tag{5.2.1}$$

We can also write this chemical equation as

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) + heat \tag{5.2.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat ($q$) is transferred *from* a system *to* its surroundings is described as exothermicA process in which heat ($q$) is transferred *from* a system *to* its surroundings.. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$heat + H_2O\,(s) \rightarrow H_2O\,(l) \tag{5.2.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermicA process in which heat q>0 is transferred *to* a system *from* its surroundings.. By convention, $q > 0$ for an endothermic reaction.

## Enthalpy of Reaction

We have stated that the change in energy ($\Delta E$) is equal to the sum of the heat produced and the work performed (Equation 9.1.3). Work done by an expanding gas is called *pressure-volume work*, also called *PV work*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$Cu\,(s) + 4HNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + 2H_2O\,(l) + 2NO_3\,(g) \tag{5.2.4}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 5.2.3 ). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure $P$ by the change in volume caused by movement of the piston ($\Delta V$). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{5.2.5}$$

The negative sign associated with *PV* work done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

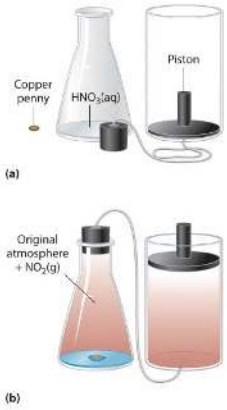



Figure 5.2.3 **An Example of Work Performed by a Reaction Carried Out at Constant Pressure***(a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of $NO_2$ gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.*

The symbol *E* in Equation 5.2.3 represents the internal energyThe sum of the kinetic and potential energies of all of a system's component. Internal energy is a state function. of a system, which is the sum of the kinetic energy and potential energy of all its components. Additionally, $\Delta E = q + w$, where *q* is the heat produced by the system and w is the work performed by the system. It is the change in internal energy that produces heat plus work. Substituting Equation 8.1.5 we find that

$$\Delta E = q - P\Delta V \tag{5.2.6}$$

Thus, if a reaction were carried out in a constant volume system (a pressure cooker for example)

$$\Delta E = q_v \tag{5.2.7}$$

Where the subscipt v in $q_v$ indicates that the process is carried out at constant volume. Thus, if the volume is held constant, the change in internal energy is equal to the heat flowing into or out of the system. However, we live in a constant pressure world, not a constant volume one. The atmospheric pressure at the surface of the earth where we live is roughly constant allowing for variation in barometric pressure due to weather or altitude.

To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (*H*)The sum of a system's internal energy *E* and the product of its pressure *P* and volume *V* (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy *E* plus the product of its pressure *P* and volume *V*:

$$H = E + PV \tag{5.2.8}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (for a given *P*, $\Delta P = 0$), the change in enthalpy ($\Delta H$)At constant pressure, the amount of heat transferred from the surroundings to the system or ΔH= q is

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta PV = \Delta E + P\Delta V \tag{5.2.9}$$

Substituting $q + w$ for $\Delta E$ (Equation 5.2.9 ) and $-w$ for $P\Delta V$ (Equation 5.2.5 ), we obtain

$$\Delta H = \Delta E + P\Delta V = q_p + w - w = q_p \tag{5.2.10}$$

The subscript *p* is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 5.2.10 we see that at constant pressure the change in enthalpy, $\Delta H$ of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{5.2.11}$$

Just as with $\Delta E$, because enthalpy is a state function, the magnitude of $\Delta H$ depends on only the initial and final states of the system, not on the path taken. The enthalpy change is the same even if the process does *not* occur at constant pressure. Most importantly, the change in enthalpy for a reaction can be determined by measuring the flow of heat into or out of the system. As we will see below, there are also cases where we want to know the amount of heat generated by a reaction, as for example for combustion of fuel. In that case knowing the molar change in enthalpy provides the information needed.

Finally, looking at Equation 9.2.9 shows that for reactions where the volume does not change, or better put does not change much, $\Delta H_{rxn} \sim \Delta E_{rxn}$. As a practical matter, this includes all reactions where all the products and reactants are either in the solid, liquid or aqueous phases. This is not generally true when there are gases on either side of the equation, a question which we will discuss in the chapter on gases.

### Note the Pattern

To find $\Delta H$, measure $q_p$.

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction ($\Delta H_{rxn}$)The change in enthalpy that occurs during a chemical reaction., the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so $\Delta H_{rxn}$ is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so $\Delta H_{rxn}$ is positive. Thus $\Delta H_{rxn} < 0$ *for an exothermic reaction*, and $\Delta H_{rxn} > 0$ *for an endothermic reaction*. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

| Reaction Type | $q$ | $\Delta H_{rxn}$ |
|---|---|---|
| exothermic | < 0 | < 0 (heat flows from a system to its surroundings) |
| endothermic | > 0 | > 0 (heat flows from the surroundings to a system) |

If $\Delta H_{rxn}$ is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (part (a) in Figure 5.2.4 ). Conversely, if $\Delta H_{rxn}$ is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (part (b) in Figure 5.2.4 ). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

### Note the Pattern

Bond breaking requires an input of energy; bond making releases energy.

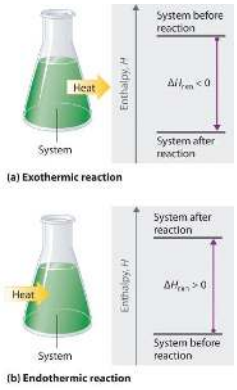



Figure \(\PageIndex{4}\) ***The Enthalpy of Reaction*** *Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, $\Delta H_{rxn}$ is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, $\Delta H_{rxn}$ is positive, and the reaction is endothermic; it is energetically uphill.*

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0 \tag{5.2.12}$$

$$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0 \tag{5.2.13}$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of Δ*H* for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 9.2.12, which describes the reaction of aluminum with iron(III) oxide ($Fe_2O_3$) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of $Al_2O_3$, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of $Fe_2O_3$ consumed:

$$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) + 815.5\ kJ \tag{5.2.14}$$

  Thus Δ*H* = −851.5 kJ/mol of $Fe_2O_3$. We can also describe Δ*H* for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 9.2.13, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) \quad \Delta H_{rxn} = -851.5\ kJ \tag{5.2.15}$$

  If 4 mol of Al and 2 mol of $Fe_2O_3$ react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{5.2.16}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 5.2.1.

### Example 5.2.1

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If Δ*H* is 6.01 kJ/mol for the reaction $H_2O(s) \rightarrow H_2O(l)$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons ($1.00 \times 10^6$ metric tons)? (A metric ton is 1000 kg.)

**Given:** energy per mole of ice and mass of iceberg

**Asked for:** energy required to melt iceberg

**Strategy:**

**A** Calculate the number of moles of ice contained in 1 million metric tons ($1.00 \times 10^6$ metric tons) of ice.

**B** Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

**Solution:**

**A** Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given Δ*H* for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by Δ*H* (+6.01 kJ/mol):

$$\begin{aligned} moles\ H_2O &= 1.00 \times 10^6\ metric\ tons H_2O \left(\frac{1000\ \cancel{kg}}{1\ \cancel{metric\ ton}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right) \\ &= 5.55 \times 10^{10}\ mol H_2O \end{aligned}$$

**B** The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55\times10^{10}\ \cancel{mol\ H_2O}\right)=3.34\times10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

| Possible sources of the approximately $3.34 \times 10^{11}$ kJ needed to melt a $1.00 \times 10^{6}$ metric ton iceberg |
|---|
| Combustion of $3.8 \times 10^{3}$ $ft^3$ of natural gas |
| Combustion of 68,000 barrels of oil |
| Combustion of 15,000 tons of coal |
| $1.1 \times 10^{8}$ kilowatt-hours of electricity |

**? Exercise 5.2.1**

If 17.3 g of powdered aluminum are allowed to react with excess $Fe_2O_3$, how much heat is produced?

**Answer**

273 kJ

## Key Equations

**definition of enthalpy**

Equation 5.2.6 : $H = E + PV$

**pressure-volume work**

Equation 5.2.5 : $w = -P\Delta V$

**enthalpy change at constant pressure**

Equation 5.2.8 : $\Delta H = \Delta E + P\Delta V$

Equation 5.2.9 : $\Delta H = q_p$

## Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**.

**Enthalpy** is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy (Δ*H*)** can be measured. A negative Δ*H* means that heat flows from a system to its surroundings; a positive Δ*H* means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction ($\Delta H_{rxn}$)** is the difference in enthalpy between products and reactants; the units of $\Delta H_{rxn}$ are kilojoules per mole. Reversing a chemical reaction reverses the sign of $\Delta H_{rxn}$. The magnitude of $\Delta H_{rxn}$ also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion ($\Delta H_{fus}$)** and the **enthalpy of vaporization ($\Delta H_{vap}$)**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion ($\Delta H_{comb}$)** is the enthalpy change that occurs when a substance is burned in excess oxygen. The **enthalpy of formation ($\Delta H_f$)** is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** ($\Delta H^o_f$) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances

present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** ($\Delta H^{o}_{rxn}$) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution ($\Delta H_{soln}$)** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

## Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

## Conceptual Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9 ) before proceeding to the Conceptual Problems.*

1. Heat implies the flow of energy from one object to another. Describe the energy flow in an

   a. exothermic reaction.

   b. endothermic reaction.

2. When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.

3. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.

   1. Water is added to sodium hydroxide pellets, and the flask becomes hot.
   2. The body metabolizes glucose, producing carbon dioxide and water.
   3. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

4. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.

   1. Concentrated acid is added to water in a flask, and the flask becomes warm.
   2. Water evaporates from your skin, causing you to shiver.
   3. A container of ammonium nitrate detonates.

5. Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.

6. Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?

7. Determine whether energy is consumed or released in each scenario. Explain your reasoning.

   1. A leaf falls from a tree.
   2. A motorboat maneuvers against a current.
   3. A child jumps rope.
   4. Dynamite detonates.
   5. A jogger sprints down a hill.

8. The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.

9. The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.

10. Is the distance a person travels on a trip a state function? Why or why not?

11.

## Contributors

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# 5.3: Hess's Law

**Learning Objectives**

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

## Hess's Law

Because enthalpy is a state function, the enthalpy change for a reaction depends on *only* two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does *not* depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, *ΔH for the net reaction is the sum of the ΔH values for the individual reactions.* This principle is called Hess's lawThe enthalpy change ΔH for an overall reaction is the sum of the ΔH values for the individual reactions., after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate Δ*H* values for reactions that are difficult to carry out directly by adding together the known Δ*H* values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 9.3.1 can be viewed as occurring in three distinct steps with known Δ*H* values. As shown in Figure 5.3.1, the first reaction produces 1 mol of solid aluminum oxide ($Al_2O_3$) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 5.3.1 ); the enthalpy change for this reaction is −732.5 kJ/mol of $Fe_2O_3$.

The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 9.3.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe).

In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 5.3.1 ); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe).

As you can see in Figure 5.3.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.3.1 gives the overall reaction, shown in part (d):

$$\begin{array}{lcll} 2Al\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \rightarrow & 2Fe\,(l,\ 1758^oC) + 2Al_2O_3\,(s,\ 1758^oC) & \Delta H = -732.5\ kJ \quad (a) \\ 2Fe\,(l,\ 1758^oC) & \rightarrow & 2Fe\,(s,\ 1758^oC) & \Delta H = -\ 27.6\ kJ \quad (b) \\ 2Fe\,(s,\ 1758^oC) + 2Al_2O_3\,(s,\ 1758^oC) & \rightarrow & 2Fe\,(l,\ 25^oC) + 2Al_2O_3\,(s,\ 25^oC) & \Delta H = -\ 91.0\ kJ \quad (c) \\ 2Al\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \rightarrow & 2Al_2O_3\,(s,\ 25^oC) + 2Fe_2O_3\,(s,\ 25^oC) & \Delta H = -852.2\ kJ \quad (d) \end{array} \tag{5.3.1}$$

The net reaction in part (d) in Equation 5.3.1 is identical to Equation 5.3.1 the sum of parts (a) + (b) +(c). By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 5.3.1.

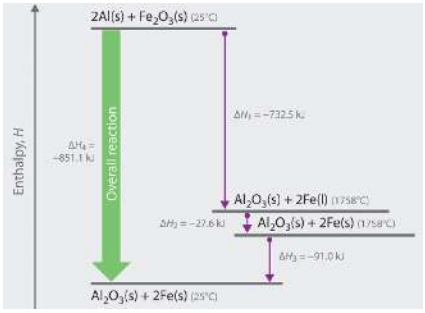



Figure 5.3.1 **Energy Changes Accompanying the Thermite Reaction** *Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of $Fe_2O_3$(s) is −851.1 kJ, whether the reaction occurs in a single step ($\Delta H_4$, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid $Al_2O_3$ and liquid iron ($\Delta H_1$), solid iron at 1758°C ($\Delta H_2$), and solid iron at 25°C ($\Delta H_3$). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.*

Comparing parts (a) and (d) in Equation 5.3.1 also illustrates an important point: *The magnitude of Δ*H *for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution).* When the product is liquid iron at its melting point (part (a) in Equation 5.3.1 ), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 9.3.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of Δ*H* for a reaction, follow this procedure:

1. Identify the equation whose Δ*H* value is unknown and write individual reactions with known Δ*H* values that, when added together, will give the desired equation.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of Δ*H* for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its Δ*H* value by that same factor.
4. Add together the individual reactions and their corresponding Δ*H* values to obtain the reaction of interest and the unknown Δ*H*.

We illustrate how to use this procedure in Example 5.3.1

### Example 5.3.1

When carbon is burned with limited amounts of oxygen gas ($O_2$), carbon monoxide (CO) is the main product:

\( \left ( 1 \right ) \;2C\left ( s \right ) + O_{2}\left ( g \right ) \rightarrow 2CO\left ( g \right ) \; \;\ \; \Delta H=-221.0 \; kJ \]

When carbon is burned in excess $O_2$, carbon dioxide ($CO_2$) is produced:

$$(2)\ C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -393.5\ kJ \tag{5.3.2}$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with $O_2$ to give $CO_2$.

**Given:** two balanced chemical equations and their Δ*H* values

**Asked for:** enthalpy change for a third reaction

**Strategy:**

**A** After balancing the chemical equation for the overall reaction, write two equations whose Δ*H* values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of Δ*H*.)

**B** Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

**Solution:**

**A** We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H_{rxn} = ? \tag{5.3.3}$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2CO\,(g) \rightarrow 2C\,(s) + O_2\,(g) \quad \Delta H = +221.0\ kJ \tag{5.3.4}$$

Because we have reversed the direction of the reaction, the sign of $\Delta H$ is changed. We can use Equation 2 as written because its product, $CO_2$, is the product we want in Equation 3:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(s) \quad \Delta H = -393.5\ kJ \tag{5.3.5}$$

**B** Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2C\,(s) + 2O_2\,(g) \rightarrow 2CO_2\,(s) \quad \Delta H = -787.0\ kJ \tag{5.3.6}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcrcrcrcl} 2CO\,(g) & \rightarrow & \cancel{2C\,(s)} + \cancel{O_2\,(g)} & \Delta H & = & -\Delta H_1 & = & +221.0\ kJ \\ \cancel{2C\,(s)} + \cancel{2}O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = & -\Delta 2H_2 & = & -787.0\ kJ \\ 2CO\,(g) + O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = & & -566.0\ kJ & \end{array} \tag{5.3.7}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with $O_2$, and the problem asks for the amount *per mole of CO*. Consequently, we must divide both sides of the final equation *and the magnitude of ΔH* by 2:

$$CO\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -283.0\ kJ \tag{5.3.8}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lrcrcrcrcl} (A) & 2C\,(s) + O_2\,(g) & \rightarrow & \cancel{2CO\,(g)} & \Delta H_A & = & \Delta H_1 & = & +221.0\ kJ \\ (B) & \cancel{2CO\,(g)} + O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H_B & & & = & ? \\ (C) & 2C\,(s) + 2O_2\,(g) & \rightarrow & 2CO_2\,(g) & \Delta H & = 2\Delta H_2 & = 2 \times (-393.5\ kJ) & = -787.0\ kJ & \end{array} \tag{5.3.9}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give $CO_2$. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given $\Delta H$ for reactions A and C. Substituting the appropriate values gives

$$\begin{array}{c} -221.0\ kJ + \Delta H_B = -787.0\ kJ \\ \Delta H_B = -566.0 \end{array} \tag{5.3.10}$$

This is again the enthalpy change for the conversion of 2 mol of CO to $CO_2$. The enthalpy change for the conversion of 1 mol of CO to $CO_2$ is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, *there may be more than one correct way to solve a problem.*

## ? Exercise 5.3.1

The reaction of acetylene ($C_2H_2$) with hydrogen ($H_2$) can produce either ethylene ($C_2H_4$) or ethane ($C_2H_6$):

$$\begin{array}{c} C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2 \\ C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2 \end{array} \tag{5.3.11}$$

What is $\Delta H$ for the reaction of $C_2H_4$ with $H_2$ to form $C_2H_6$?

**Answer**

−136.3 kJ/mol of $C_2H_4$

## Enthalpies of Reaction

Chapter 7 and Chapter 8 presented a wide variety of chemical reactions, and you learned how to write balanced chemical equations that include all the reactants and the products except heat. One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion ($\Delta H_{comb}$)The change in enthalpy that occurs during a combustion reaction.: Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion ($\Delta H_{fus}$)The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance.: The enthalpy change that accompanies the melting, or *fusion*, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization ($\Delta H_{vap}$)The enthalpy change that accompanies the vaporization of 1 mol of a substance.: The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution ($\Delta H_{soln}$)The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent.: The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

**Table 5.3.1 Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points**

| Substance | $\Delta H_{vap}$ (kJ/mol) | $\Delta H_{fus}$ (kJ/mol) |
|---|---|---|
| argon (Ar) | 6.3 | 1.3 |
| methane ($CH_4$) | 9.2 | 0.84 |
| ethanol ($CH_3CH_2OH$) | 39.3 | 7.6 |
| benzene ($C_6H_6$) | 31.0 | 10.9 |
| water ($H_2O$) | 40.7 | 6.0 |
| mercury (Hg) | 59.0 | 2.29 |
| iron (Fe) | 340 | 14 |

### Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

### Summary

For a chemical reaction, the **enthalpy of reaction ($\Delta H_{rxn}$)** is the difference in enthalpy between products and reactants; the units of $\Delta H_{rxn}$ are kilojoules per mole. Reversing a chemical reaction reverses the sign of $\Delta H_{rxn}$. The magnitude of $\Delta H_{rxn}$ also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion ($\Delta H_{fus}$)** and the **enthalpy of vaporization ($\Delta H_{vap}$)**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion ($\Delta H_{comb}$)** is the enthalpy change that occurs when a substance is burned in excess oxygen.

### Key Takeaway

- Hess's law: The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions:

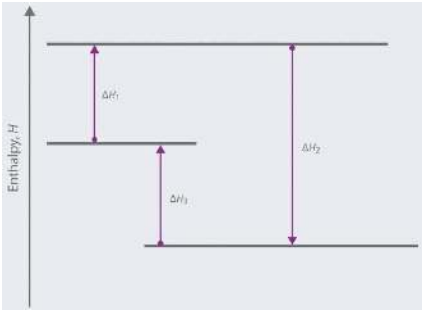
## Conceptual Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9 ) before proceeding to the Conceptual Problems.*

1. Based on the following energy diagram,

   a. write an equation showing how the value of $\Delta H_2$ could be determined if the values of $\Delta H_1$ and $\Delta H_3$ are known.

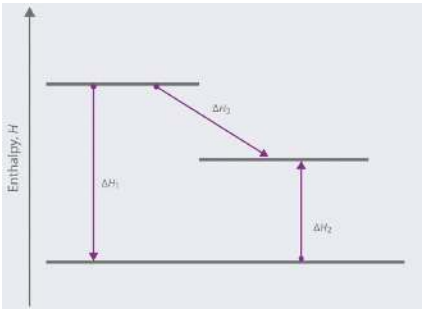
   b; identify each step as being exothermic or endothermic.




2. Based on the following energy diagram,

   a. write an equation showing how the value of $\Delta H_3$ could be determined if the values of $\Delta H_1$ and $\Delta H_2$ are known.

   b. identify each step as being exothermic or endothermic.




3. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
4. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
   1. the melting of a solid
   2. the conversion of a gas to a liquid
   3. the solidification of a liquid
   4. the dissolution of a solid into water
5. In their elemental form, $A_2$ and $B_2$ exist as diatomic molecules. Given the following reactions, each with an associated $\Delta H°$, describe how you would calculate $\Delta H^o_f$ for the compound $AB_2$.

$$\begin{array}{lcll} 2AB & \rightarrow & A_2 + B_2 & \Delta H_1^o \\ 3AB & \rightarrow & AB_2 + A_2B & \Delta H_2^o \\ 2A_2B & \rightarrow & 2A_2 + B_2 & \Delta H_3^o \end{array} \tag{5.3.12}$$

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.*

1. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

| Fuel | $\Delta H^o_{combustion}$(kJ/mol) | Density (g/mL) |
|---|---|---|
| methanol | −726.1 | 0.791 |
| 2,2,4-trimethylpentane | −5461.4 | 0.692 |

2. a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

| Fuel | $\Delta H^o_{combustion}$(kJ/mol) |
|---|---|
| methanol | −726.1 |
| 1-ethyl-2-methylbenzene | −5210.2 |
| *n*-octane | −5470.5 |

   b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.

3. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

| Fuel | $\Delta H^o_f$(kJ/mol) |
|---|---|
| ethanol | −1366.8 |
| benzene | −3267.6 |
| cyclooctane | −5434.7 |

## Answers

1.

2.

a. To one decimal place

methanol: $\Delta H$/g = −22.6 kJ

$C_9H_{12}$: $\Delta H$/g = −43.3 kJ

octane: $\Delta H$/g = −47.9 kJ

Octane provides the largest amount of heat per gram upon combustion.

b, $\Delta H_f(C_9H_{17})$ = −46.1 kJ/mol

## Contributors

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# 5.4: Heats of Formation

**Learning Objectives**

- To understand Enthalpies of Formation and be able to use them to calculated Enthalpies of Reaction

## Enthalpies of Formation

Chapter 3 and Chapter 4 presented a wide variety of chemical reactions, and you learned how to write balanced chemical equations that include all the reactants and the products except heat. One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

- Enthalpy of formation ($\Delta H_f$)The enthalpy change for the formation of 1 mol of a compound from its component elements.: The enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The corresponding relationship is

$$elements \rightarrow compound \qquad \Delta H_{rxn} = \Delta H_f \tag{5.4.1}$$

For example,

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{rxn} = \Delta H_f\,[CO_2\,(g)] \tag{5.4.2}$$

The sign convention for $\Delta H_f$ is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

### Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

## Standard Enthalpies of Formation

The magnitude of $\Delta H$ for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditionsThe conditions under which most thermochemical data are tabulated: 1 atm for all gases and a concentration of 1.0 M for all species in solution. for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard stateThe most stable form of a pure substance at a pressure of 1 atm at a specified temperature.. This is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called standard enthalpies of formation ($\Delta H^o_f$)The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition. (which is pronounced "delta H eff naught"). *The standard enthalpy of formation of any element in its standard state is zero by definition*. For example, although oxygen can exist as ozone ($O_3$), atomic oxygen (O), and molecular oxygen ($O_2$), $O_2$ is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is $H_2$(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 5.4.1 ). Therefore, $O_2$(g), $H_2$(g), and graphite have $\Delta H^o_f$ values of zero.



Figure 5.4.1 **Elemental Carbon** *Although graphite and diamond are both forms of elemental carbon, graphite is more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.*

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{5.4.3}$$

It is not possible to measure the value of $\Delta H^o_f$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, $O_2$, and $H_2$ and measuring the heat evolved as glucose is formed; the reaction shown in Equation 5.4.3 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of are obtained using Hess's law and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of $\Delta H^o_f$ for an extensive list of compounds are given in the Reference Tables. Note that $\Delta H^o_f$ values are always reported in kilojoules per mole of the substance of interest. Also notice in the Reference Tables that the standard enthalpy of formation of $O_2$(g) is zero because it is the most stable form of oxygen in its standard state.

### Example 5.4.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

1. HCl(g)
2. $MgCO_3$(s)
3. $CH_3(CH_2)_{14}CO_2H$(s) (palmitic acid)

**Given:** compound

**Asked for:** balanced chemical equation for its formation from elements in standard states

**Strategy:**

Use Appendix A to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

**Solution:**

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in the Reference Tables by a $\Delta H^o_f$ value of 0 kJ/mol.

1. Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2$(g) and $Cl_2$(g), respectively, the unbalanced chemical equation is $H_2$(g) + $Cl_2$(g) → HCl(g)

   Fractional coefficients are required in this case because $\Delta H^o_f$ values are reported for *1 mol* of the product, HCl. Multiplying both $H_2$(g) and $Cl_2$(g) by 1/2 balances the equation:

   $$\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) \rightarrow HCl\,(g)$$

2. The standard states of the elements in this compound are Mg(s), C(s, graphite), and $O_2$(g). The unbalanced chemical equation is thus Mg(s) + C(s, graphite) + $O_2$(g) → $MgCO_3$(s)

   This equation can be balanced by inspection to give

$$Mg\,(g) + C\,(s, graphite)\,\frac{3}{2}O_2\,(g) \rightarrow MgCO_3\,(s)$$

3. Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows: C(s, graphite) + $H_2$(g) + $O_2$(g) → $CH_3(CH_2)_{14}CO_2H$(s)

   There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

   16C(s, graphite) + 16$H_2$(g) + $O_2$(g) → $CH_3(CH_2)_{14}CO_2H$(s)

**? Exercise 5.4.1**

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

1. NaCl(s)
2. $H_2SO_4$(l)
3. $CH_3CO_2H$(l) (acetic acid)

**Answer**

1. $$Na\,(g) + \frac{1}{2}Cl_2\,(g) \rightarrow NaCl\,(s)$$
2. $$H_2\,(g) + \frac{1}{8}S_8\,(s) + 2O_2\,(g) \rightarrow H_2SO_4\,(l)$$
3. 2C(s) + $O_2$(g) + 2$H_2$(g) → $CH_3CO_2H$(l)

## Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose $\Delta H_f^o$ values are known. The standard enthalpy of reaction ($\Delta H_{rxn}$)The enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard state. is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{5.4.4}$$

where A, B, C, and D are chemical substances and *a*, *b*, *c*, and *d* are their stoichiometric coefficients. The magnitude of $\Delta H^o$ is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underset{reactants}{\left[c\Delta H^o_f\,(C) + d\Delta H^o_f\,(D)\right]} - \underset{products}{\left[a\Delta H^o_f\,(A) + b\Delta H^o_f\,(B)\right]} \tag{5.4.5}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants) \tag{5.4.6}$$

where the symbol Σ means “sum of” and *m* and *n* are the stoichiometric coefficients of each of the products and the reactants, respectively. “Products minus reactants” summations such as Equation 5.4.6 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, “products minus reactants” summations are very common in chemistry; we will encounter many others in subsequent chapters.

### Note the Pattern

Products minus reactants” summations are typical of state functions.

To demonstrate the use of tabulated $\Delta H^o$ values, we will use them to calculate $\Delta H_{rxn}$ for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O_6\,(s) + O_2\,(g) \rightarrow CO_2\,(g) + 6H_2O\,(l) \tag{5.4.7}$$

Using Equation 5.4.6, we write

$$\begin{aligned} &\Delta H_f^o \\ &= \left\{6\Delta H_f^o\,[CO_2\,(g)] + 6\Delta H_f^o\,[H_2O\,(g)]\right\} - \left\{6\Delta H_f^o\,[C_6H_{12}O_6\,(s)] + 6\Delta H_f^o\,[O_2\,(g)]\right\} \end{aligned} \tag{5.4.8}$$

From the Reference Tables, the relevant $\Delta H^o_f$ values are $\Delta H^o_f\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 9.4.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\begin{aligned} \Delta H^o_{comb} &= [6\,(-393.5\ kJ/mol) + 6\,(-285.8\ kJ/mol)] \\ &- [-1273.3 + 6\,(0\ kJ/mol)] = -2802.5\ kJ/mol \end{aligned} \tag{5.4.9}$$

As illustrated in Figure 5.4.3, we can use Equation 5.4.9 to calculate $\Delta H^o_f$ for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled $\Delta H^o_{comb}$ The alternative hypothetical pathway consists of four separate reactions that convert the reactants *to the elements* in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the $\Delta H^o_f$ values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned} \Delta H_1^o &= \Delta H_f^o\,[glucose\,(s)] = -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) = +1273.3\ kJ \\ \Delta H_2^o &= 6\Delta H_f^o\,[O_2\,(g)] = 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) = 0\ kJ \end{aligned} \tag{5.4.10}$$

(Recall that when we reverse a reaction, we must also reverse the sign of the accompanying enthalpy change.) The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of $O_2$) to the elements is therefore +1273.3 kJ.

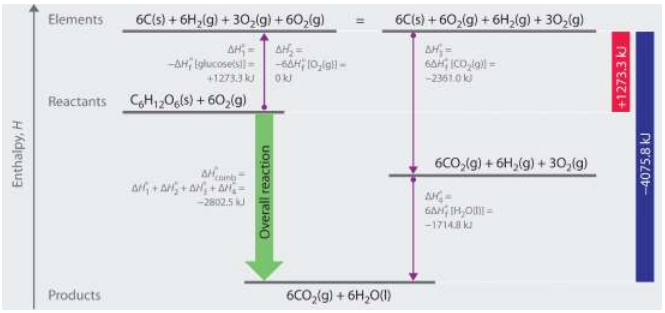



Figure 5.4.2 **A Thermochemical Cycle for the Combustion of Glucose** Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled $\Delta H^o_{comb}$ indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled $\Delta H^o_1$ and $\Delta H^o_2$ ). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled $\Delta H^o_3$ and $\Delta H^o_4$ ). Because enthalpy is a state function, $\Delta H^o_{comb}$ is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 5.4.2 ) are identical to those used to define the $\Delta H^o_f$ values of the products. Consequently, the enthalpy changes (from the Reference Tables) are

$$\begin{aligned} \Delta H_3^o &= \Delta H_f^o\,[CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ \\ \Delta H_4^o &= 6\Delta H_f^o\,[H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \end{aligned} \tag{5.4.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{5.4.12}$$

This is the same result we obtained using the "products minus reactants" rule and $\Delta H^o_f$ values. The two results must be the same because Equation 5.4.11 is just a more compact way of describing the thermochemical cycle shown in Figure 5.4.2.

## Example 5.4.2

Long-chain fatty acids such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] are one of the two major sources of energy in our diet ($\Delta H^o f$ =−891.5 kJ/mol). Use the data in the Reference Table to calculate $\Delta H^o_{comb}$ for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

**Given:** compound and $\Delta H^o f$ values

**Asked for:** $\Delta H^o_{comb}$ per mole and per gram

**Strategy:**

**A** After writing the balanced chemical equation for the reaction, use Equation 5.4.6 and the values from the Reference Table to calculate $\Delta H^o_{comb}$ the energy released by the combustion of 1 mol of palmitic acid.

**B** Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 5.4.9 for the combustion of glucose to determine which is the better fuel.

**Solution:**

**A** To determine the energy released by the combustion of palmitic acid, we need to calculate its $\Delta H^o_f$ As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_2\,(s) + 23O_2\,(g) \rightarrow 16CO_2\,(g) + 16H_2)\,(l) \tag{5.4.13}$$

Using Equation 9.4.5 ("products minus reactants") with $\Delta H^o_f$ values from the Reference Table (and omitting the physical states of the reactants and products to save space) gives

$$\Delta H^o_{comb} = \sum m\Delta H^o{}_f\,(products) - \sum n\Delta H^o{}_f\,(reactants)$$

$$= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\ )]$$

$$-\,[-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\ )]$$

$$= -9977.3\ kJ/mol$$

This is the energy released by the combustion of 1 mol of palmitic acid.

**B** The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 5.4.9, $\Delta H^o f$ of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

**? Exercise 5.4.2**

Use the data in Appendix A to calculate $\Delta H^{o}_{rxn}$ for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain $H_2$(g):

$$\underset{water-gas\ shift\ reaction}{\left(CO\left(g\right)+H_2O\left(g\right)\rightarrow CO_2\left(g\right)+H_2\left(g\right)\right)}$$

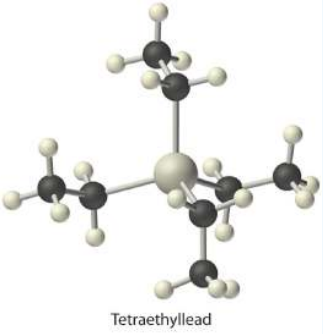
**Answer**

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's $\Delta H^{o}f$ which we cannot obtain otherwise. This procedure is illustrated in Example 3.

**✔ Example 5.4.3**

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $CO_2$(g), $H_2O$(l), and red PbO(s). What is the standard enthalpy of formation of tetraethyllead, given that $\Delta H^{o}f$ is −19.29 kJ/g for the combustion of tetraethyllead and $\Delta H^{o}f$ of red PbO(s) is −219.0 kJ/mol?


Tetraethyllead

**Given:** reactant, products, and $\Delta H^{o}_{comb}$ values

**Asked for:** $\Delta H^{o}_{f}$ of the reactants

**Strategy:**

**A** Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 9.4.4 to get the equation for $\Delta H^{o}_{f}$ of tetraethyl lead.

**B** Convert $\Delta H^{o}_{comb}$ per gram given in the problem to $\Delta H^{o}_{comb}$ per mole by multiplying $\Delta H^{o}_{comb}$ per gram by the molar mass of tetraethyllead.

**C** Use the Reference Table to obtain values of $\Delta H^{o}_{f}$ for the other reactants and products. Insert these values into the equation for $\Delta H^{o}_{f}$ of tetraethyl lead and solve the equation.

**Solution:**

**A** The balanced chemical equation for the combustion reaction is as follows:

$$\left(C_2H_5\right)_4Pb\left(l\right)+27O_2\left(g\right)\rightarrow 2PbO\left(s\right)+16CO_2\left(g\right)+20H_2O\left(l\right) \tag{5.4.14}$$

Using Equation 5.4.6 gives

$$\Delta H^{o}_{comb} = \left[2\Delta H^{o}_{f}\left(PbO\right)+16\Delta H^{o}_{f}\left(CO_2\right)+20\Delta H^{o}_{f}\left(H_2O\right)\right]-\left[2\Delta H^{o}_{f}\left(\left(C_2H_5\right)_4Pb\right)+27\Delta H^{o}_{f}\left(O_2\right)\right]$$

Solving for $\Delta H^{o}_{f}$ [$(C_2H_5)4Pb$] gives

$$\Delta H^o_f\left((C_2H_5)_4\,Pb\right) = \Delta H^o_f\left(PbO\right) + 8\Delta H^o_f\left(CO_2\right) + 10\Delta H^o_f\left(H_2O\right) - \frac{27}{2}\Delta H^o_f\left(O_2\right) - \frac{\Delta H^o_{comb}}{2}$$

The values of all terms other than $\Delta H^o_f\,[(C_2H_5)4Pb]$ are given in the Reference Table

**B** The magnitude of $\Delta H^o_{comb}$ is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get $\Delta H^o_{comb}$ for 1 mol of tetraethyl lead:

$$\Delta H^o_{comb} = \left(\frac{-1929\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right) = -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, $\Delta H^o_{rxn}$ is

$$\Delta H^o_{rxn} = 2\ \cancel{mol\ (C_2H5)_4\,Pb}\left(\frac{-6929\ kJ}{1\ \cancel{mol\ (C_2H5)_4\,Pb}}\right) = -12,480\ kJ$$

**C** Inserting the appropriate values into the equation for $\Delta H^o_f\,[(C_2H_5)4Pb]$ gives

$$\begin{aligned}\Delta H^o_f\left[(C_2H_4)_4\,Pb\right] &= \left[1\ mol\ PbO\ \times 219.0\ kJ/mol\right] + \left[8\ mol\ CO_2 \times (-393.5\ kJ/mol)\right] \\ &\quad + \left[10\ mol\ H_2O \times (-285.8\ kJ/mol)\right] + \left[-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2\right] \\ &\quad \left[12,480.2\ kJ/mol\ \ (C_2H_5)_4\,Pb\right] \\ &= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol\end{aligned}$$

## Exercise 5.4.3

Ammonium sulfate $[(NH_4)_2SO_4]$ is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$

The value of $\Delta H^o_{rxn}$ is −2805 kJ/g $H_2SO_4$. Use the data in Appendix A to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

**Answer**

−1181 kJ/mol

## Key Equations

**relationship between $\Delta H^o_{rxn}$ and $\Delta H^o_f$**

Equation 5.4.6 : $\Delta H^o_{rxn} = \Sigma\Delta H^o_f(\text{products}) - \Delta H^o_f(\text{reactants})$

## Summary

The **enthalpy of formation ($\Delta H_f$)** is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** ($\Delta H^o_f$) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** ($\Delta H^o_{rxn}$) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution ($\Delta H_{soln}$)** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

## Key Takeaways

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 °C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

## Conceptual Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.4.9 ) before proceeding to the Conceptual Problems.*

1. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
2. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
3. What is the difference between $\Delta H^{o}_{f}$ and $\Delta H_{f}$?
4. How can $\Delta H^{o}_{f}$ of a compound be determined if the compound cannot be prepared by the reactions used to define its standard enthalpy of formation?
5. For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.
   a. HBr
   b. $CH_3OH$
   c. $NaHCO_3$
6. Describe the distinction between $\Delta H_{soln}$ and $\Delta H_{f}$.
7. The following table lists $\Delta H^{o}_{soln}$ values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

| Compound | $\Delta H^{o}_{soln}$(kJ/mol) |
|---|---|
| KOH | −57.61 |
| $LiNO_3$ | −2.51 |
| $KMnO_4$ | 43.56 |
| $NaC_2H_3O_2$ | −17.32 |

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.4.9 ) before proceeding to the Numerical Problems.*

1. Using "Appendix A, calculate $\Delta H^{o}_{rxn}$ for each chemical reaction.
   a. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
   b. $CaCO_3(s, \text{calcite}) \rightarrow CaO(s) + CO_2(g)$
   c. $AgNO_3(s) + NaCl(s) \rightarrow AgCl(s) + NaNO_3(s)$
2. Using "Appendix A, determine $\Delta H^{o}_{rxn}$ for each chemical reaction.
   a. $2Na(s) + Pb(NO_3)_2(s) \rightarrow 2NaNO_3(s) + Pb(s)$
   b. $Na_2CO_3(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(l)$
   c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
3. Calculate $\Delta H^{o}_{rxn}$ for each chemical equation. If necessary, balance the chemical equations.
   a. $Fe(s) + CuCl_2(s) \rightarrow FeCl_2(s) + Cu(s)$
   b. $(NH_4)_2SO_4(s) + Ca(OH)_2(s) \rightarrow CaSO_4(s) + NH_3(g) + H_2O(l)$
   c. $Pb(s) + PbO_2(s) + H_2SO_4(l) \rightarrow PbSO_4(s) + H_2O(l)$
4. Calculate $\Delta H^{o}_{rxn}$ for each reaction. If necessary, balance the chemical equations.

a. $4HBr(g) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$

b. $2KBr(s) + H_2SO_4(l) \rightarrow K_2SO_4(s) + 2HBr(g)$

c. $4Zn(s) + 9HNO_3(l) \rightarrow 4Zn(NO_3)_2(s) + NH_3(g) + 3H_2O(l)$

5. Use the data in "Appendix A to calculate $\Delta H^o_f$ for the reaction $Sn(s, white) + 4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$.
6. Use the data in "Appendix A to calculate $\Delta H^o_f$ for the reaction $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$.
7. How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas?
8. How much energy is released or consumed if 10.0 g of $N_2O_5$ is completely decomposed to produce gaseous nitrogen dioxide and oxygen?
9. In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

   $NaCl(s) + H_2SO_4(l) + MnO_2(s) \rightarrow Na_2SO_4(s) + MnCl_2(s) + H_2O(l) + Cl_2(g)$

   Calculate $\Delta H^o_{rxn}$ for this reaction. Is the reaction exothermic or endothermic?
10. Would you expect heat to be evolved during each reaction?

    1. solid sodium oxide with gaseous sulfur dioxide to give solid sodium sulfite
    2. solid aluminum chloride reacting with water to give solid aluminum oxide and hydrogen chloride gas
11. How much heat is released in preparing an aqueous solution containing 6.3 g of calcium chloride, an aqueous solution containing 2.9 g of potassium carbonate, and then when the two solutions are mixed together to produce potassium chloride and calcium carbonate?
12.

## Answers

1. a. −1203 kJ/mol $O_2$

   b. 179.2 kJ

   c. −59.3 kJ
2.
3.
4.
5. −174.1 kJ/mol
6.
7. −20.3 kJ
8.
9. −34.3 kJ/mol $Cl_2$; exothermic
10.
11. $\Delta H$ = −2.86 kJ $CaCl_2$: −4.6 kJ; $K_2CO_3$, −0.65 kJ; mixing, −0.28 kJ

## Contributors

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# 5.5: Enthalpies of Solution

**Learning Objectives**

- To understand Enthalpies of Solution and be able to use them to calculate the Heat absorbed or emitted when making solutions.

## Enthalpies of Solution and Dilution

Physical changes, such as melting or vaporization, and chemical reactions, in which one substance is converted to another, are accompanied by changes in enthalpy. Two other kinds of changes that are accompanied by changes in enthalpy are the dissolution of solids and the dilution of concentrated solutions.

The dissolution of a solid can be described as follows:

$$solute\,(s) + solvent\,(l) \rightarrow soulution\,(l) \tag{5.5.1}$$

The values of $\Delta H_{soln}$ for some common substances are given in Table 5.5.1. The sign and the magnitude of $\Delta H_{soln}$ depend on specific attractive and repulsive interactions between the solute and the solvent; these factors will be discussed in Chapter 13. When substances dissolve, the process can be either exothermic ($\Delta H_{soln} < 0$) or endothermic ($\Delta H_{soln} > 0$), as you can see from the data in Table 5.5.1.

**Table 5.5.1 Enthalpies of Solution at 25°C of Selected Ionic Compounds in Water (in kJ/mol)**

| | **Anion** | | | | |
|---|---|---|---|---|---|
| **Cation** | Fluoride | Chloride | Bromide | Iodide | Hydroxide |
| lithium | 4.7 | −37.0 | −48.8 | −63.3 | −23.6 |
| sodium | 0.9 | 3.9 | −0.6 | −7.5 | −44.5 |
| potassium | −17.7 | 17.2 | 19.9 | 20.3 | −57.6 |
| ammonium | −1.2 | 14.8 | 16.8 | 13.7 | — |
| silver | −22.5 | 65.5 | 84.4 | 112.2 | — |
| magnesium | −17.7 | −160.0 | −185.6 | −213.2 | 2.3 |
| calcium | 11.5 | −81.3 | −103.1 | −119.7 | −16.7 |
| | | | | | |
| | Nitrate | Acetate | Carbonate | Sulfate | |
| lithium | −2.5 | — | −18.2 | −29.8 | |
| sodium | 20.5 | −17.3 | −26.7 | 2.4 | |
| potassium | 34.9 | −15.3 | −30.9 | 23.8 | |
| ammonium | 25.7 | −2.4 | — | 6.6 | |
| silver | 22.6 | — | 22.6 | 17.8 | |
| magnesium | −90.9 | — | −25.3 | −91.2 | |
| calcium | −19.2 | — | −13.1 | −18.0 | |

Substances with large positive or negative enthalpies of solution have commercial applications as instant cold or hot packs. Single-use versions of these products are based on the dissolution of either calcium chloride ($CaCl_2$, $\Delta H_{soln}$ = −81.3 kJ/mol) or ammonium

nitrate ($NH_4NO_3$, $\Delta H_{soln}$ = +25.7 kJ/mol). Both types consist of a plastic bag that contains about 100 mL of water plus a dry chemical (40 g of $CaCl_2$ or 30 g of $NH_4NO_3$) in a separate plastic pouch. When the pack is twisted or struck sharply, the inner plastic bag of water ruptures, and the salt dissolves in the water. If the salt is $CaCl_2$, heat is released to produce a solution with a temperature of about 90°C; hence the product is an "instant hot compress." If the salt is $NH_4NO_3$, heat is absorbed when it dissolves, and the temperature drops to about 0° for an "instant cold pack."

A similar product based on the *precipitation* of sodium acetate, not its dissolution, is marketed as a reusable hand warmer (Figure 5.5.1 ). At high temperatures, sodium acetate forms a highly concentrated aqueous solution. With cooling, an unstable *supersaturated* solution containing excess solute is formed. When the pack is agitated, sodium acetate trihydrate [$CH_3CO_2Na{\cdot}3H_2O$] crystallizes, and heat is evolved:

$$Na^+(aq) + CH_3CO_2^-(aq) + H_2O(l) \rightarrow CH_3CO_2Na \cdot \bullet H_2O(s) \quad (5.5.2)$$
$$\Delta H = -\Delta H_{soln} = -19.7\ kJ/mol$$

A bag of concentrated sodium acetate solution can be carried until heat is needed, at which time vigorous agitation induces crystallization and heat is released. The pack can be reused after it is immersed in hot water until the sodium acetate redissolves.




Figure 5.5.1 **An Instant Hot Pack Based on the Crystallization of Sodium Acetate** *The hot pack is at room temperature prior to agitation (left). Because the sodium acetate is in solution, you can see the metal disc inside the pack. After the hot pack has been agitated, the sodium acetate crystallizes (right) to release heat. Because of the mass of white sodium acetate that has crystallized, the metal disc is no longer visible.*

The amount of heat released or absorbed when a substance is dissolved is not a constant; it depends on the final concentration of the solute. The $\Delta H_{soln}$ values given previously and in Table 5.5.1 for example, were obtained by measuring the enthalpy changes at various concentrations and extrapolating the data to infinite dilution.

Because $\Delta H_{soln}$ depends on the concentration of the solute, diluting a solution can produce a change in enthalpy. If the initial dissolution process is exothermic ($\Delta H < 0$), then the dilution process is also exothermic. This phenomenon is particularly relevant for strong acids and bases, which are often sold or stored as concentrated aqueous solutions. If water is added to a concentrated solution of sulfuric acid (which is 98% $H_2SO_4$ and 2% $H_2O$) or sodium hydroxide, the heat released by the large negative $\Delta H$ can cause the solution to boil. Dangerous spattering of strong acid or base can be avoided if the concentrated acid or base is slowly added to water, so that the heat liberated is largely dissipated by the water. Thus you should **never add water to a strong acid or base**; a useful way to avoid the danger is to remember: *Add water to acid and get blasted!*

## Summary

The **enthalpy of solution ($\Delta H_{soln}$)** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

## Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

## Conceptual Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Conceptual Problems.*

1. Describe the distinction between $\Delta H_{soln}$ and $\Delta H_f$.
2. Does adding water to concentrated acid result in an endothermic or an exothermic process?
3. The following table lists $\Delta H^o_{soln}$ values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

| Compound | $\Delta H^o_{soln}$(kJ/mol) |
|---|---|
| KOH | −57.61 |
| $LiNO_3$ | −2.51 |
| $KMnO_4$ | 43.56 |
| $NaC_2H_3O_2$ | −17.32 |

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9 ) before proceeding to the Numerical Problems.*

## Answers

## Contributors

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# 5.6: Calorimetry

**Learning Objectives**

- To use calorimetric data to calculate enthalpy changes.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. CalorimetryA set of techniques used to measure enthalpy changes in chemical (reactions) and physical changes (melting for example) processes. describes a set of techniques employed to measure enthalpy changes in chemical (reactions) and physical(melting for example) processes using devices called *calorimeters*.

To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

## Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred ($q$) and the *heat capacity* of the object. Its heat capacity ($C$)J/$^{o}$C. The amount of energy needed to raise the temperature of an object 1°C. The units of heat capacity are joules per degree Celsius is the amount of energy needed to raise the temperature of the object exactly 1°C; the units of $C$ are joules per degree Celsius (J/°C).

Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, and perhaps a bit more correctly in SI, as joules per Kelvin, J/K

The change in temperature ($\Delta T$) is

$$\Delta T = \frac{q}{C} \tag{5.6.1}$$

where $q$ is the amount of heat (in joules), $C$ is the heat capacity (in joules per degree Celsius), and $\Delta T$ is $T_{\text{final}} - T_{\text{initial}}$ (in degrees Celsius). Note that $\Delta T$ is *always* written as the final temperature minus the initial temperature.

Since Kelvin and degrees Celcius are exactly the same the DIFFERENCE $\Delta T = T_{\text{final}} - T_{\text{initial}}$ is the same whether one uses Kelving (K) or Celcius (°C) for BOTH $T_{\text{final}}$ and $T_{\text{initial}}$ , but make sure not to mix these two temperature units.

The value of $C$ is intrinsically a positive number because it is defined as energy necessary to RAISE the temperature, but $\Delta T$ and $q$ can be either positive or negative, and they both must have the *same* sign. If $\Delta T$ and $q$ are positive, then *heat flows from the surroundings into an object*. If $\Delta T$ and $q$ are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity ($C_{\text{p}}$) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C. The units of $C_{\text{p}}$ are thus J/(mol·°C).The subscript $p$ indicates that the value was measured at constant pressure. The specific heat ($C_{\text{s}}$) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C. Its units are thus J/(g·°C). We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change in two ways:

$$q = nC_p\Delta T \tag{5.6.2}$$

$$q = mC_s\Delta T \tag{5.6.3}$$

The specific heats of some common substances are given in Table 5.6.1 Note that the specific heat values of most solids are less than 1 J/(g·°C), whereas those of most liquids are about 2 J/(g·°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g·°C), is one of the highest known.

**Table 5.6.1 Specific Heats of Selected Substances at 25°C**

| Compound | Specific Heat [J/(g·°C)] |
|---|---|
| $H_2O(l)$ | 4.184 |
| $H_2O(g)$ | 2.062 |
| $CH_3OH$ (methanol) | 2.531 |
| $CH_3CH_2OH$ (ethanol) | 2.438 |
| *n*-$C_6H_{14}$ (*n*-hexane) | 2.270 |
| $C_6H_6$ (benzene) | 1.745 |
| C(s) (graphite) | 0.709 |
| C(s) (diamond) | 0.509 |
| Al(s) | 0.897 |
| Fe(s) | 0.449 |
| Cu(s) | 0.385 |
| Au(s) | 0.129 |
| Hg(l) | 0.140 |
| NaCl(s) | 0.864 |
| MgO(s) | 0.921 |
| $SiO_2$(s) (quartz) | 0.742 |
| $CaCO_3$(s) (calcite) | 0.915 |

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected (Figure 5.6.1 ). Water's capacity to absorb large amounts of energy without undergoing a large increase in temperature also explains why swimming pools and waterbeds are usually heated. Heat must be applied to raise the temperature of the water to a comfortable level for swimming or sleeping and to maintain that level as heat is exchanged with the surroundings. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1°C. Consequently, the mechanism for maintaining our body temperature at about 37°C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

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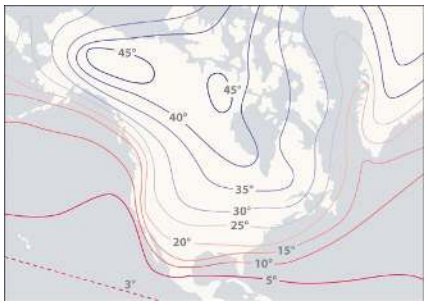



Figure 5.6.1 **The High Specific Heat of Liquid Water Has Major Effects on Climate** *Regions that are near very large bodies of water, such as oceans or lakes, tend to have smaller temperature differences between summer and winter months than regions in the center of a continent. The contours on this map show the difference between January and July monthly mean surface temperatures (in degrees Celsius).*

## Example 5.6.1

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)




**Passive solar system.** *During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.*

**Given:** volume and density of water and initial and final temperatures

**Asked for:** amount of energy stored

**Strategy:**

**A** Use the density of water at 22.0°C to obtain the mass of water (*m*) that corresponds to 400 L of water. Then compute Δ*T* for the water.

**B** Determine the amount of heat absorbed by substituting values for *m*, $C_s$, and Δ*T* into Equation 5.6.1

**Solution:**

**A** The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) = 3.99 \times 10^5 g\ H_2O$$

The temperature change (Δ*T*) is 38.0°C − 22.0°C = +16.0°C.

**B** From Table 5.6.1, the specific heat of water is 4.184 J/(g·°C). From Equation 5.6.3 the heat absorbed by the water is thus

$$q = mC_s\Delta T = \left(3.99X10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)\left(16.0\ \cancel{^oC}\right) = 2.67 \times 10^7 J = 2.67 \times 10^4 kJ$$

Both *q* and Δ*T* are positive, consistent with the fact that the water has absorbed energy.

## Exercise 5.6.1

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the

rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz ($SiO_2$) in Table 5.6.1.

**Answer**

$2.7 \times 10^4$ kJ (Even though the mass of sandstone is more than six times the mass of the water in Example 7, the amount of thermal energy stored is the same to two significant figures.)

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0 \tag{5.6.4}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{5.6.5}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

### Note the Pattern

Substituting for $q$ from Equation 5.6.2 gives

$$[mC_s\Delta T]_{hot} + [mC_s\Delta T]_{hot} = 0 \tag{5.6.6}$$

which can be rearranged to give

$$[mC_s\Delta T]_{hot} = -[mC_s\Delta T]_{hot} \tag{5.6.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 5.6.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

### Example 5.6.2

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

**Given:** mass and initial temperature of two objects

**Asked for:** final temperature

**Strategy:**

Using Equation 5.6.6 and writing $\Delta T$ as $T_{\text{final}} - T_{\text{initial}}$ for both the copper and the water, substitute the appropriate values of $m$, $C_s$, and $T_{\text{initial}}$ into the equation and solve for $T_{\text{final}}$.

**Solution:**

We can adapt Equation 5.6.7 to solve this problem, remembering that $\Delta T$ is defined as $T_{\text{final}} - T_{\text{initial}}$:

$$[mC_s\,(T_{final} - T_{initial})]_{Cu} + [mC_s\,(T_{final} - T_{initial})]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 5.6.1 gives

$$[(30\ g)\,(0.385\ J)\,(T_{final} - T_{initial})]_{Cu} + [mC_s\,(T_{final} - T_{initial})]_{H_2O} = 0$$

$$T_{final}\,(11.6\ J/^oC) - 924\ J + T_{final}\,(418.4\ J/^oC) - 11,300\ J$$

$$T_{final}\,(430\ J/\,(g\cdot^o\,C)) = -12,224\ J$$

$$T_{final} = -28.4\ ^oC$$

Exercise (a)

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

**? Exercise 5.6.2**

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

**Answer**

80.0°C

## Measuring Heat Flow

In Example 7, radiant energy from the sun was used to raise the temperature of water. A calorimetric experiment uses essentially the same procedure, except that the thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

## Constant-Pressure Calorimetry

Because $\Delta H$ is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeterA device used to measure enthalpy changes in chemical processes at constant pressure. give $\Delta H$ values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure 5.6.2 ), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree ($10^{-6}$°C). Because the heat released or absorbed at constant pressure is equal to $\Delta H$, the relationship between heat and $\Delta H_{rxn}$ is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{5.6.8}$$

The use of a constant-pressure calorimeter is illustrated in Example 3.

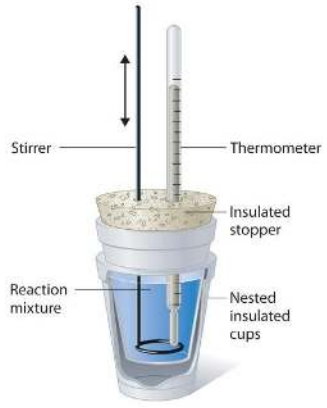



Figure 5.6.2 **A Coffee-Cup Calorimeter** *This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.*

## Example 5.6.3

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm$^3$. What is $\Delta H_{soln}$ (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

**Given:** mass of substance, volume of solvent, and initial and final temperatures

**Asked for:** $\Delta H_{soln}$

**Strategy:**

**A** Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.

**B** Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 5.6.8.

**C** Use the molar mass of KOH to calculate $\Delta H_{soln}$.

**Solution:**

**A** To calculate $\Delta H_{soln}$, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$(100.0\ mL\ H2O)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

**B** Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$q_{calorimater} = mC_s\Delta T = \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(11.7\ ^oC) = 5130\ J = 5.13\ lJ$$

The temperature of the solution increased because heat was absorbed by the solution ($q$ > 0). Where did this heat come from? It was released by KOH dissolving in water. From Equation 5.6.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

**C** The last step is to use the molar mass of KOH to calculate $\Delta H_{soln}$—the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) = -57.2\ kJ/mol$$

## Exercise 5.6.3

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 9, find $\Delta H_{soln}$ for $NH_4Br$ (in kilojoules per mole).

**Answer**

16.6 kJ/mol

## Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-

volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown schematically in Figure 9.6.3). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

Figure 9.6.3 A Bomb Calorimeter *After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.*

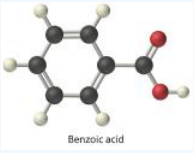
Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. As we noted in Chapter 9.2 the heat released by a reaction carried out at constant volume is identical to the change in *internal energy* ($\Delta E$) rather than the enthalpy change ($\Delta H$); $\Delta E$ is related to $\Delta H$ by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta E < \Delta H$, the relationship between the measured temperature change and $\Delta H_{\text{comb}}$ is given in Equation 5.6.9, where $C_{\text{bomb}}$ is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{5.6.9}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{\text{comb}}$ = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used in Equation 5.6.9 to determine $C_{\text{bomb}}$. The use of a bomb calorimeter to measure the $\Delta H_{\text{comb}}$ of a substance is illustrated in Example 10.

### Example 5.6.4

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the $\Delta H_{\text{comb}}$ of glucose?




**Given:** mass and $\Delta T$ for combustion of standard and sample

**Asked for:** $\Delta H_{\text{comb}}$ of glucose

**Strategy:**

**A** Calculate the value of $q_{rxn}$ for benzoic acid by multiplying the mass of benzoic acid by its $\Delta H_{comb}$. Then determine the heat capacity of the calorimeter ($C_{bomb}$) from $q_{comb}$ and $\Delta T$.

**B** Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the $\Delta H_{comb}$ of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

**Solution:**

The first step is to use Equation 5.6.9 and the information obtained from the combustion of benzoic acid to calculate $C_{bomb}$. We are given $\Delta T$, and we can calculate $q_{comb}$ from the mass of benzoic acid:

$$qcomb = \left(0.579 \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ$$

From Equation 5.6.9,

$$-Cbomb = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC$$

**B** According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ$$

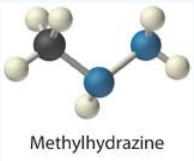
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the $\Delta H_{comb}$ of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb}$ = −2803 kJ/mol that calculated using enthalpies of formation.

## ? Exercise 5.6.4

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine ($CH_3NHNH_2$) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the $\Delta H_{comb}$ of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

**Answer**

$-1.30 \times 10^3$ kJ/mol

### Key Equations

**relationship of quantity of a substance, heat capacity, heat flow, and temperature change**

Equation 5.6.2 : $q = nC_p\Delta T$

Equation 5.6.3 : $q = mC_s\Delta T$

**constant-pressure calorimetry**

Equation 5.6.8 : $\Delta H_{rxn} = q_{rxn} = -q_{calorimeter} = -mC_s\Delta T$

**constant-volume calorimetry**

Equation 5.6.9 : $\Delta H_{comb} < q_{comb} = -q_{calorimeter} = -C_{bomb}\Delta T$

## Summary

**Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat ($C_s$)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity ($C_p$)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives $\Delta H$ values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

## Key Takeaway

- Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system.

## Conceptual Problems

1. Can an object have a negative heat capacity? Why or why not?
2. What two factors determine the heat capacity of an object? Does the specific heat also depend on these two factors? Explain your answer.
3. Explain why regions along seacoasts have a more moderate climate than inland regions do.
4. Although soapstone is more expensive than brick, soapstone is frequently the building material of choice for fireplaces, particularly in northern climates with harsh winters. Propose an explanation for this.

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.*

1. Using Equation 5.6.2 and Equation 5.6.3, derive a mathematical relationship between $C_s$ and $C_p$.
2. Complete the following table for 28.0 g of each element at an initial temperature of 22.0°C.

| Element | $q$ (J) | $C_p$ [J/(mol·K)] | Final $T$ (°C) |
|---|---|---|---|
| nickel | 137 | 26.07 | |
| silicon | | 19.789 | 3.0 |
| zinc | 603 | | 77.5 |
| mercury | 137 | | 57 |

3. Using Table 9.6.1, how much heat is needed to raise the temperature of a 2.5 g piece of copper wire from 20°C to 80°C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount? If you were using one of these metals to channel heat away from electrical components, which metal would you use? Once heated, which metal will cool faster? Give the specific heat for each metal.
4. Gold has a molar heat capacity of 25.418 J/(mol·K), and silver has a molar heat capacity of 23.350 J/(mol·K).
    1. If you put silver and gold spoons of equal mass into a cup of hot liquid and wait until the temperature of the liquid is constant, which spoon will take longer to cool down when removed from the hot liquid?
    2. If 8.00 g spoons of each metal at 20.0°C are placed in an insulated mug with 50.0 g of water at 97.0°C, what will be the final temperature of the water after the system has equilibrated? (Assume that no heat is transferred to the surroundings.)
5. In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150 mL of water 7.5°C? Explain how this process illustrates the law of conservation of energy.

6. How much heat must be evolved by a reaction to raise the temperature of 8.0 oz of water 5.0°C? What mass of lithium iodide would need to be dissolved in this volume of water to produce this temperature change?
7. A solution is made by dissolving 3.35 g of an unknown salt in 150 mL of water, and the temperature of the water rises 3.0°C. The addition of a silver nitrate solution results in a precipitate. Assuming that the heat capacity of the solution is the same as that of pure water, use the information in Table 9.5.1 and solubility rules to identify the salt.
8. Using the data in Table 9.8.2, calculate the change in temperature of a calorimeter with a heat capacity of 1.78 kJ/°C when 3.0 g of charcoal is burned in the calorimeter. If the calorimeter is in a 2 L bath of water at an initial temperature of 21.5°C, what will be the final temperature of the water after the combustion reaction (assuming no heat is lost to the surroundings)?
9. A 3.00 g sample of TNT (trinitrotoluene, $C_7H_5N_3O_6$) is placed in a bomb calorimeter with a heat capacity of 1.93 kJ/°C; the $\Delta H_{comb}$ of TNT is −3403.5 kJ/mol. If the initial temperature of the calorimeter is 19.8°C, what will be the final temperature of the calorimeter after the combustion reaction (assuming no heat is lost to the surroundings)? What is the $\Delta H_f$ of TNT?

## Answers

1. $C_p = C_s \times$ (molar mass)
2. 
3. For Cu: $q$ = 58 J; For Al: $q$ = 130 J; Even though the values of the molar heat capacities are very similar for the two metals, the specific heat of Cu is only about half as large as that of Al, due to the greater molar mass of Cu versus Al: $C_s$ = 0.385 and 0.897 *J*/(g·K) for Cu and Al, respectively. Thus loss of one joule of heat will cause almost twice as large a decrease in temperature of Cu versus Al.
4. 
5. 4.7 kJ
6. 
7. $\Delta H_{soln}$ = −0.56 kJ/g; based on reaction with $AgNO_3$, salt contains halide; dividing $\Delta H_{soln}$ values in Table 5.2 by molar mass of salts gives lithium bromide as best match, with −0.56 kJ/g.
8. 
9. $T_{final}$ = 43.1°C; the combustion reaction is

$$4C_7H_5N_3O_{6(s)} + 21O_{2(g)} \rightarrow 28CO_{2(g)} + 10H_2O_{(g)} + 6N_{2(g)}$$

with

$$\Delta_f^\circ H(TNT) = -65.5\ kJ/mol$$

## Contributors

- Anonymous

Modified by Joshua Halpern

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# 5.7: Thermochemistry and Nutrition

**Learning Objectives**

- To understand the relationship between thermochemistry and nutrition.

The thermochemical quantities that you probably encounter most often are the caloric values of food. Food supplies the raw materials that your body needs to replace cells and the energy that keeps those cells functioning. About 80% of this energy is released as heat to maintain your body temperature at a sustainable level to keep you alive.

The nutritional CalorieA unit used to indicate the caloric content of food. It is equal to 1 kilocalorie (1 kcal). (with a capital C) that you see on food labels is equal to 1 kcal (kilocalorie). The caloric content of food is determined from its enthalpy of combustion ($\Delta H_{comb}$) per gram, as measured in a bomb calorimeter, using the general reaction

$$food + excess\ O_2(g) \rightarrow CO_2(g) + H_2O(l) + N_2(g) \tag{5.7.1}$$

There are two important differences, however, between the caloric values reported for foods and the $\Delta H_{comb}$ of the same foods burned in a calorimeter. First, the $\Delta H_{comb}$ described in joules (or kilojoules) are negative for all substances that can be burned. In contrast, the caloric content of a food is always expressed as a *positive* number because it is *stored energy*. Therefore,

$$caloric\ content = -\Delta H_{comb} \tag{5.7.2}$$

Second, when foods are burned in a calorimeter, any nitrogen they contain (largely from proteins, which are rich in nitrogen) is transformed to $N_2$. In the body, however, nitrogen from foods is converted to urea [$(H_2N)_2C{=}O$], rather than $N_2$ before it is excreted. The $\Delta H_{comb}$ of urea measured by bomb calorimetry is −632.0 kJ/mol. Consequently, the enthalpy change measured by calorimetry for any nitrogen-containing food is greater than the amount of energy the body would obtain from it. The difference in the values is equal to the $\Delta H_{comb}$ of urea multiplied by the number of moles of urea formed when the food is broken down. This point is illustrated schematically in the following equations:

$$food + excess\ O_2\,(g) \xrightarrow{\Delta H_1<0} CO_2\,(g) + H_2O\,(l) + \cancel{(H_2N)_2C{=}O\,(s)} \tag{5.7.3}$$

$$\cancel{(H_2N)_2C{=}O\,(s)} + \cancel{excess}\ \frac{3}{2}O_2\,(g) \xrightarrow{\Delta H_2=632.0\ kJ/mol} CO_2\,(g) + 2H_2O\,(l) + N_2\,(g) \tag{5.7.4}$$

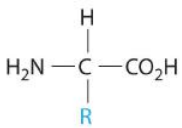
which adds up to

$$food + excess\ O_2\,(g) \xrightarrow{\Delta H_3=\Delta H_1+\Delta H_2<0} 2CO_2\,(g) + 3H_2O\,(l) + N_2\,(g) \tag{5.7.5}$$

All three $\Delta H$ values are negative, and, by Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. The magnitude of $\Delta H_1$ must be less than $\Delta H_3$, the calorimetrically measured $\Delta H_{comb}$ for a food. By producing urea rather than $N_2$, therefore, humans are excreting some of the energy that was stored in their food.




Because of their different chemical compositions, foods vary widely in caloric content. As we saw in Example 5, for instance, a fatty acid such as palmitic acid produces about 39 kJ/g during combustion, while a sugar such as glucose produces 15.6 kJ/g. Fatty acids and sugars are the building blocks of fats and carbohydrates, respectively, two of the major sources of energy in the diet. Nutritionists typically assign average values of 38 kJ/g (about 9 Cal/g) and 17 kJ/g (about 4 Cal/g) for fats and carbohydrates, respectively, although the actual values for specific foods vary because of differences in composition. Proteins, the third major source of calories in the diet, vary as well. Proteins are composed of amino acids, which have the following general structure:

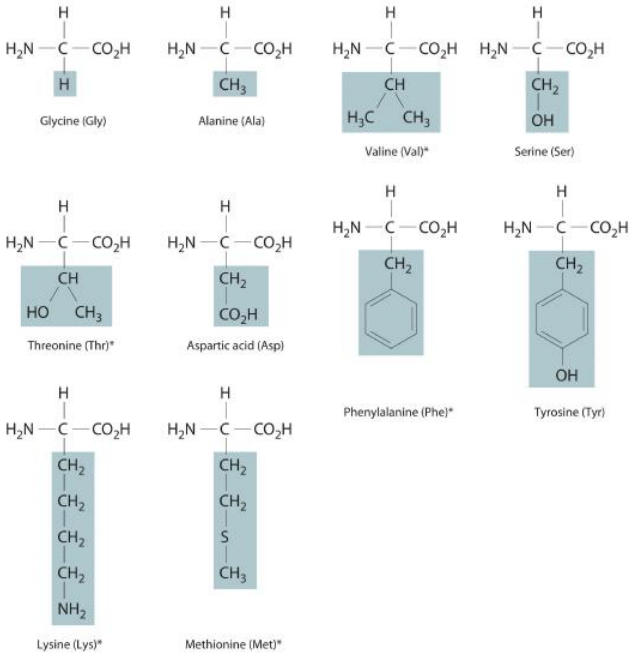



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**General structure of an amino acid.** An amino acid contains an amine group ($-NH_2$) and a carboxylic acid group ($-CO_2H$).

In addition to their amine and carboxylic acid components, amino acids may contain a wide range of other functional groups: R can be hydrogen (–H); an alkyl group (e.g., $-CH_3$); an aryl group (e.g., $-CH_2C_6H_5$); or a substituted alkyl group that contains an amine, an alcohol, or a carboxylic acid (Figure 5.7.1 ). Of the 20 naturally occurring amino acids, 10 are required in the human diet; these 10 are called *essential amino acids* because our bodies are unable to synthesize them from other compounds. Because R can be any of several different groups, each amino acid has a different value of $\Delta H_{comb}$. Proteins are usually estimated to have an average $\Delta H_{comb}$ of 17 kJ/g (about 4 Cal/g).

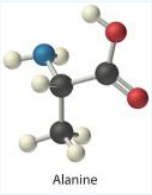
**Figure 5.7.1 The Structures of 10 Amino Acids**




*Essential amino acids in this group are indicated with an asterisk.*

**Example 5.7.1**

Calculate the amount of available energy obtained from the biological oxidation of 1.000 g of alanine (an amino acid). Remember that the nitrogen-containing product is urea, not $N_2$, so biological oxidation of alanine will yield *less* energy than will combustion. The value of $\Delta H_{comb}$ for alanine is −1577 kJ/mol.




**Given:** amino acid and $\Delta H_{comb}$ per mole

**Asked for:** caloric content per gram

**Strategy:**

**A** Write balanced chemical equations for the oxidation of alanine to $CO_2$, $H_2O$, and urea; the combustion of urea; and the combustion of alanine. Multiply both sides of the equations by appropriate factors and then rearrange them to cancel urea from both sides when the equations are added.

**B** Use Hess's law to obtain an expression for $\Delta H$ for the oxidation of alanine to urea in terms of the $\Delta H_{comb}$ of alanine and urea. Substitute the appropriate values of $\Delta H_{comb}$ into the equation and solve for $\Delta H$ for the oxidation of alanine to $CO_2$, $H_2O$, and urea.

**C** Calculate the amount of energy released per gram by dividing the value of $\Delta H$ by the molar mass of alanine.

**Solution:**

The actual energy available biologically from alanine is less than its $\Delta H_{comb}$ because of the production of urea rather than $N_2$. We know the $\Delta H_{comb}$ values for alanine and urea, so we can use Hess's law to calculate $\Delta H$ for the oxidation of alanine to $CO_2$, $H_2O$, and urea.

**A** We begin by writing balanced chemical equations for (1) the oxidation of alanine to $CO_2$, $H_2O$, and urea; (2) the combustion of urea; and (3) the combustion of alanine. Because alanine contains only a single nitrogen atom, whereas urea and $N_2$ each contain two nitrogen atoms, it is easier to balance Equations 1 and 3 if we write them for the oxidation of 2 mol of alanine:

$$(1)\quad 2C_3H_7NO_2\,(s) + 6O_2\,(g) \rightarrow 5CO_2\,(g) + 5H_2O\,(l) + (H_2N)_2\,C=O\,(s)$$

$$(2)\quad (H_2N)_2\,C=O\,(s) + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s) + \frac{15}{2}O_2\,(g) \rightarrow 6CO_2\,(g) + 7H_2O\,(l) + N_2\,(g)$$

Adding Equations 1 and 2 and canceling urea from both sides give the overall chemical equation directly:

$$(1)\quad 2C_3H_7NO_2\,(s) + 6O_2\,(g) \rightarrow 5CO_2\,(g) + 5H_2O\,(l) + \cancel{(H_2N)_2\,C=O\,(s)}$$

$$\cancel{(2)\quad (H_2N)_2\,C=O\,(s)} + \frac{3}{2}O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s) + \frac{15}{2}O_2\,(g) \rightarrow 6CO_2\,(g) + 7H_2O\,(l) + N_2\,(g)$$

**B** By Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. We know that $\Delta H_3 = 2\Delta H_{comb}$ (alanine), $\Delta H_2 = \Delta H_{comb}$ (urea), and $\Delta H_1 = 2\Delta H$ (alanine → urea). Rearranging and substituting the appropriate values gives

$$\Delta H_1 = \Delta H_3 - \Delta H_2$$

$$= 2\,(-1577\ kJ/mol) - (-632.0\ kJ/mol)$$

= -2522 \; kJ/\left ( 2 \;mol\; analine \right ) \notag \]

Thus $\Delta H$ (alanine → urea) = −2522 kJ/(2 mol of alanine) = −1261 kJ/mol of alanine. Oxidation of alanine to urea rather than to nitrogen therefore results in about a 20% decrease in the amount of energy released (−1261 kJ/mol versus −1577 kJ/mol).

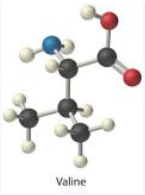
**C** The energy released per gram by the biological oxidation of alanine is

$$\left(\frac{-1261\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{89.094\ g}\right) = -14.15\ kJ/g$$

This is equal to −3.382 Cal/g.

## ? Exercise 5.7.1

Calculate the energy released per gram from the oxidation of valine (an amino acid) to $CO_2$, $H_2O$, and urea. Report your answer to three significant figures. The value of $\Delta H_{comb}$ for valine is −2922 kJ/mol.




**Answer**

−22.2 kJ/g (−5.31 Cal/g)

The reported caloric content of foods does not include $\Delta H_{comb}$ for those components that are not digested, such as fiber. Moreover, meats and fruits are 50%−70% water, which cannot be oxidized by $O_2$ to obtain energy. So water contains no calories. Some foods contain large amounts of fiber, which is primarily composed of sugars. Although fiber can be burned in a calorimeter just like glucose to give carbon dioxide, water, and heat, humans lack the enzymes needed to break fiber down into smaller molecules that can be oxidized. Hence fiber also does not contribute to the caloric content of food.

We can determine the caloric content of foods in two ways. The most precise method is to dry a carefully weighed sample and carry out a combustion reaction in a bomb calorimeter. The more typical approach, however, is to analyze the food for protein, carbohydrate, fat, water, and "minerals" (everything that doesn't burn) and then calculate the caloric content using the average values for each component that produces energy (9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals). An example of this approach is shown in Table 5.7.1 for a slice of roast beef. The compositions and caloric contents of some common foods are given in Table 5.7.2

**Table 5.7.1 Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef**

| Composition | Calories |
|---|---|
| 97.5 g of water | × 0 Cal/g = 0 |
| 58.7 g of protein | × 4 Cal/g = 235 |
| 69.3 g of fat | × 9 Cal/g = 624 |
| 0 g of carbohydrates | × 4 Cal/g = 0 |
| 1.5 g of minerals | × 0 Cal/g = 0 |
| **Total mass: 227.0 g** | **Total calories: about 900 Cal** |

**Table 5.7.2 Approximate Compositions and Fuel Values of Some Common Foods**

| Food (quantity) | Approximate Composition (%) | | | | Food Value (Cal/g) | Calories |
|---|---|---|---|---|---|---|
| | **Water** | **Carbohydrate** | **Protein** | **Fat** | | |
| beer (12 oz) | 92 | 3.6 | 0.3 | 0 | 0.4 | 150 |
| coffee (6 oz) | 100 | ~0 | ~0 | ~0 | ~0 | ~0 |
| milk (1 cup) | 88 | 4.5 | 3.3 | 3.3 | 0.6 | 150 |
| egg (1 large) | 75 | 2 | 12 | 12 | 1.6 | 80 |
| butter (1 tbsp) | 16 | ~0 | ~0 | 79 | 7.1 | 100 |
| apple (8 oz) | 84 | 15 | ~0 | 0.5 | 0.6 | 125 |
| bread, white (2 slices) | 37 | 48 | 8 | 4 | 2.6 | 130 |
| brownie (40 g) | 10 | 55 | 5 | 30 | 4.8 | 190 |
| hamburger (4 oz) | 54 | 0 | 24 | 21 | 2.9 | 326 |
| fried chicken (1 drumstick) | 53 | 8.3 | 22 | 15 | 2.7 | 195 |
| carrots (1 cup) | 87 | 10 | 1.3 | ~0 | 0.4 | 70 |

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope (Table 5.7.3 ). A moderately active individual requires about 2500−3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

**Table** 5.7.3 **Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities**

| Activity | Cal/h |
|---|---|
| sleeping | 80 |
| driving a car | 120 |
| standing | 140 |
| eating | 150 |
| walking 2.5 mph | 210 |
| mowing lawn | 250 |
| swimming 0.25 mph | 300 |
| roller skating | 350 |
| tennis | 420 |
| bicycling 13 mph | 660 |
| running 10 mph | 900 |

### Example 5.7.2

What is the minimum number of Calories expended by a 72.6 kg person who climbs a 30-story building? (Assume each flight of stairs is 14 ft high.) How many grams of glucose are required to supply this amount of energy? (The energy released during the combustion of glucose was calculated in Example 5.)

**Given:** mass, height, and energy released by combustion of glucose

**Asked for:** calories expended and mass of glucose needed

**Strategy:**

**A** Convert mass and height to SI units and then substitute these values into Equation 5.7.6 to calculate the change in potential energy (in kilojoules). Divide the calculated energy by 4.184 Cal/kJ to convert the potential energy change to Calories.

**B** Use the value obtained in Example 1 for the combustion of glucose to calculate the mass of glucose needed to supply this amount of energy.

**Solution:**

The energy needed to climb the stairs equals the difference between the person's potential energy (*PE*) at the top of the building and at ground level.

**A** Recall that $PE = mgh$. Because $m$ and $h$ are given in non-SI units, we must convert them to kilograms and meters, respectively

Thus

$$PE = (72.6\ kg)\,(9.81\ m/s^2)\,(128m) = 8.55 \times 10^4\,(kg \cdot m^2/s^2) = 91.2kJ$$

To convert to Calories, we divide by 4.184 kJ/kcal:

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ kcal}{4.184\ \cancel{kJ}}\right) = 21.8\ kcal = 21.8\ Cal$$

**B** Because the combustion of glucose produces 15.6 kJ/g (Example 5), the mass of glucose needed to supply 85.5 kJ of energy is

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ g\ glucose}{15.6\ \cancel{kJ}}\right) = 5.85\ g\ glucose$$

This mass corresponds to only about a teaspoonful of sugar! Because the body is only about 30% efficient in using the energy in glucose, the actual amount of glucose required would be higher: (100%/30%) × 5.85 g = 19.5 g. Nonetheless, this calculation illustrates the difficulty many people have in trying to lose weight by exercise alone.

**? Exercise 5.7.2**

Calculate how many times a 160 lb person would have to climb the tallest building in the United States, the 110-story Willis Tower in Chicago, to burn off 1.0 lb of stored fat. Assume that each story of the building is 14 ft high and use a calorie content of 9.0 kcal/g of fat.

**Answer**

About 55 times

The calculations in Example2 ignore various factors, such as how fast the person is climbing. Although the rate is irrelevant in calculating the change in potential energy, it is very relevant to the amount of energy actually required to ascend the stairs. The calculations also ignore the fact that the body's conversion of chemical energy to mechanical work is significantly less than 100% efficient. According to the average energy expended for various activities listed in Table 5.7.1, a person must run more than 4.5 h at 10 mph or bicycle for 6 h at 13 mph to burn off 1 lb of fat (1.0 lb × 454 g/lb × 9.0 Cal/g = 4100 Cal). But if a person rides a bicycle at 13 mph for only 1 h per day 6 days a week, that person will burn off 50 lb of fat in the course of a year (assuming, of course, the cyclist doesn't increase his or her intake of calories to compensate for the exercise).

## Summary

The nutritional **Calorie** is equivalent to 1 kcal (4.184 kJ). The caloric content of a food is its $\Delta H_{comb}$ per gram. The combustion of nitrogen-containing substances produces $N_2(g)$, but the biological oxidation of such substances produces urea. Hence the actual energy available from nitrogen-containing substances, such as proteins, is less than the $\Delta H_{comb}$ of urea multiplied by the number of moles of urea produced. The typical caloric contents for food are 9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals.

## Key Takeaway

- Thermochemical concepts can be applied to determine the actual energy available in food.

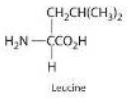
## Conceptual Problems

1. Can water be considered a food? Explain your answer.
2. Describe how you would determine the caloric content of a bag of popcorn using a calorimeter.
3. Why do some people initially feel cold after eating a meal and then begin to feel warm?
4. In humans, one of the biochemical products of the combustion/digestion of amino acids is urea. What effect does this have on the energy available from these reactions? Speculate why conversion to urea is preferable to the generation of $N_2$.

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.7.9) before proceeding to the Numerical Problems.*

1. Determine the amount of energy available from the biological oxidation of 1.50 g of leucine (an amino acid, $\Delta H_{comb}$ = −3581.7 kJ/mol).




2. Calculate the energy released (in kilojoules) from the metabolism of 1.5 oz of vodka that is 62% water and 38% ethanol by volume, assuming that the total volume is equal to the sum of the volume of the two components. The density of ethanol is

0.824 g/mL. What is this enthalpy change in nutritional Calories?

3. While exercising, a person lifts an 80 lb barbell 7 ft off the ground. Assuming that the transformation of chemical energy to mechanical energy is only 35% efficient, how many Calories would the person use to accomplish this task? From Figure 5.7.2, how many grams of glucose would be needed to provide the energy to accomplish this task?
4. A 30 g sample of potato chips is placed in a bomb calorimeter with a heat capacity of 1.80 kJ/°C, and the bomb calorimeter is immersed in 1.5 L of water. Calculate the energy contained in the food per gram if, after combustion of the chips, the temperature of the calorimeter increases to 58.6°C from an initial temperature of 22.1°C.

## Contributors

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# 5.8: Energy Sources and the Environment

**Learning Objectives**

- To use thermochemical concepts to discuss environmental issues.

Our contemporary society requires the constant expenditure of huge amounts of energy to heat our homes, provide telephone and cable service, transport us from one location to another, provide light when it is dark outside, and run the machinery that manufactures material goods. The United States alone consumes almost $10^6$ kJ per person per day, which is about 100 times the normal required energy content of the human diet. This figure is about 30% of the world's total energy usage, although only about 5% of the total population of the world lives in the United States.

In contrast, the average energy consumption elsewhere in the world is about $10^5$ kJ per person per day, although actual values vary widely depending on a country's level of industrialization. In this section, we describe various sources of fossil fuel energy and their impact on the environment.

Driven by environmental concerns about climate change and pollution, the world is undergoing a transformation from fossil fuels to renewable resources such as solar, and wind. The role that hydro and nuclear energy will play is uncertain and especially in the later case a policy rather than a scientific issue.

## Fossil Fuels

According to the law of conservation of energy, energy can never actually be "consumed"; it can only be changed from one form to another.

Fossil fuels, coal, oil and natural gas are the result of anaerobic decay of dead plants and animals laid down hundreds of millions of years ago, most of which took place well before the dinosaurs strode the earth. Fossil fuels slowly formed as further geological layers compressed and heated the dead organic matter. The energy content of fossil fuels results from the transformation of sunlight into vegetation and the chemical transformation brought about by anaerobic cooking at high pressures and temperatures over geological times.

Figure 5.8.1 represents a plant for generating electricity using oil or coal where the fuel is burned in a boiler, superheating steam which then powers a turbine for electrical generation. Oil derived fuels are seldom used in large power plants but diesel is used commonly in small electrical generators either in remote locations or as back up for when electrical distribution systems fail. Natural gas fueled power plants burn the fuel directly in the turbine which is similar to a jet engine. Coal power plants can convert ~40% of the energy released from combustion to electricity. In comparison, nuclear power plants can be more than 50% efficient and gas turbines can approach 60% mostly due to higher operating temperatures. Co-generation, using the plant to produce not only electricity but also heat for industrial or other purposes can raise overall efficiency by 10 - 15 % or so.

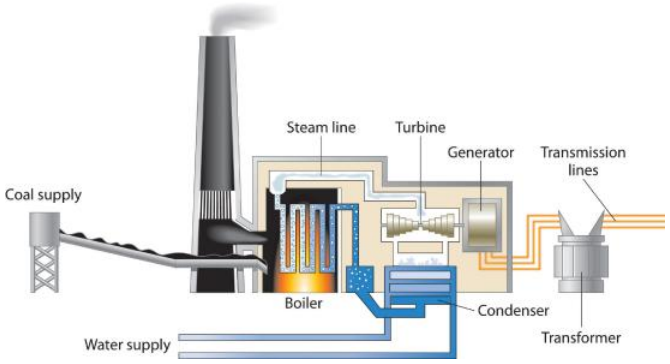



Figure 5.8.1 **Electricity from Coal** *A coal-powered electric power plant uses the combustion of coal to produce steam, which drives a turbine to produce electricity.*

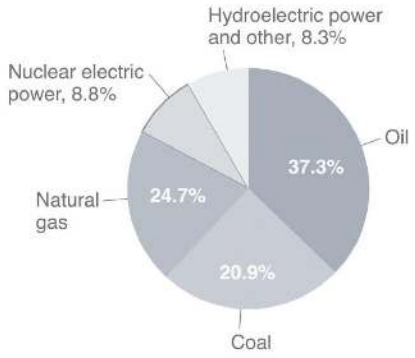
The total expenditure of energy in the world each year is about $3 \times 10^{17}$ kJ. Today, more than 80% of this energy is provided by the combustion of fossil fuels: oil, coal, and natural gas (The sources of the energy consumed in the United States in 2009 are shown in Figure 5.8.2 ) but as Table 5.8.1 from the Wikipedia shows, energy usage is a complex issue. Petroleum dominates as a source of

energy for transportation because gasoline is easy to transport, but is very little used for electrical generation, whereas 91% of coal is used for electrical generation. The other major use of coal is as a reducing agent for metal refining from ores. The former is called thermal coal, the latter metallurgical coal.

**Table** 5.8.1 **: Energy useage in the United States for 2008**

| Supply Sources | Percent of Source | Demand Sectors | Percent of Sector |
|---|---|---|---|
| Petroleum<br>37.1% | 71% Transportation<br>23% Industrial<br>5% Residential and Commercial<br>1% Electric Power | Transportation<br>27.8% | 95% Petroleum<br>2% Natural Gas<br>3% Renewable Energy |
| Natural Gas<br>23.8% | 3% Transportation<br>34% Industrial<br>34% Residential and Commercial<br>29% Electric Power | Industrial<br>20.6% | 42% Petroleum<br>40% Natural Gas<br>9% Coal<br>10% Renewable Energy |
| Coal<br>22.5% | 8% Industrial<br><1% Residential and Commercial<br>91% Electric Power | Residential and Commercial<br>10.8% | 16% Petroleum<br>76% Natural Gas<br>1% Coal<br>1% Renewable Energy |
| Renewable Energy<br>7.3% | 11% Transportation<br>28% Industrial<br>10% Residential and Commercial<br>51% Electric Power | Electric Power<br>40.1% | 1% Petroleum<br>17% Natural Gas<br>51% Coal<br>9% Renewable Energy<br>21% Nuclear Electric Power |
| Nuclear Electric Power<br>8.5% | 100% Electric Power | | |

**Figure** 5.8.2 **Energy Consumption in the United States by Source, 2009**




*More than 80% of the total energy expended is provided by the combustion of fossil fuels, such as oil, coal, and natural gas.*

## Coal

CoalA complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. It is used as a fuel. was primarily laid down from the large swamp forests of the Carboniferous Period. Coal deposits are found today where those forests were Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. Because plants contain large amounts of *cellulose*, derived from linked glucose units, the structure of

coal is more complex than that of petroleum (Figure 5.8.3 ). In particular, coal contains a large number of oxygen atoms that link parts of the structure together, in addition to the basic framework of carbon–carbon bonds. It is impossible to draw a single structure for coal; however, because of the prevalence of rings of carbon atoms (due to the original high cellulose content), coal is more similar to an aromatic hydrocarbon than an aliphatic one.

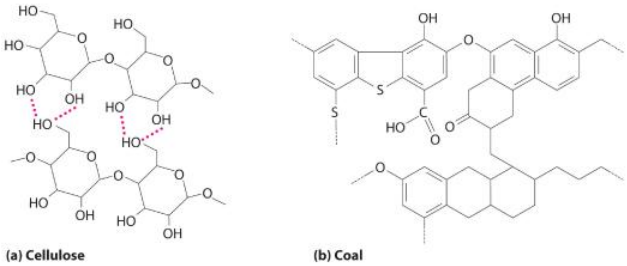



Figure 5.8.3 **The Structures of Cellulose and Coal** *(a) Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. (b) When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing coal. This drawing shows some of the common structural features of coal; note the presence of many different kinds of ring structures.*

There are four distinct classes of coal (Table 5.8.21 ); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. Lignite, with a hydrogen:carbon ratio of about 1.0 and a high oxygen content, has the lowest $\Delta H_{comb}$. Lignite is extensively mined in Germany and Poland. Anthracite, in contrast, with a hydrogen:carbon ratio of about 0.5 and the lowest oxygen content, has the highest $\Delta H_{comb}$ and is the highest grade of coal. Anthracite is the first choice for metallurgical refining. The most abundant form in the Western United States in anthracite while that in the Eastern United States is bituminous coal, which has a high sulfur content because of the presence of small particles of pyrite ($FeS_2$). Combustion of coal releases the sulfur in $FeS_2$ as $SO_2$, which is a major contributor to acid rain. Table 5.8.3 compares the $\Delta H_{comb}$ per gram of oil, natural gas, and coal with those of selected organic compounds.

**Table 5.8.2 Properties of Different Types of Coal**

| Type | % Carbon | Hydrogen:Carbon Mole Ratio | % Oxygen | % Sulfur | Heat Content | US Deposits |
|---|---|---|---|---|---|---|
| anthracite | 92 | 0.5 | 3 | 1 | high | Pennsylvania, New York |
| bituminous | 80 | 0.6 | 8 | 5 | medium | Appalachia, Midwest, Utah |
| subbituminous | 77 | 0.9 | 16 | 1 | medium | Rocky Mountains |
| lignite | 71 | 1.0 | 23 | 1 | low | Montana |

**Table 5.8.3 Enthalpies of Combustion of Common Fuels and Selected Organic Compounds**

| Fuel | $\Delta H_{comb}$ (kJ/g) |
|---|---|
| dry wood | −15 |
| peat | −20.8 |
| bituminous coal | −28.3 |
| charcoal | −35 |
| kerosene | −37 |
| $C_6H_6$ (benzene) | −41.8 |
| crude oil | −43 |
| natural gas | −50 |
| $C_2H_2$ (acetylene) | −50.0 |
| $CH_4$ (methane) | −55.5 |
| gasoline | −84 |
| hydrogen | −143 |

Peat, a precursor to coal, is the partially decayed remains of plants that grow in the swampy areas of the Carboniferous Period. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. Even though peat is a smoky, poor-burning fuel that gives off relatively little heat, humans have burned it since ancient times (Figure 5.8.4 ). If a peat bog were buried under many layers of sediment for a few million years, the peat would eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.



Figure 5.8.4 **A Peat Bog** *Peat is a smoky fuel that burns poorly and produces little heat, but it has been used as a fuel since ancient times.*

## Converting Coal to Gaseous and Liquid Fuels

As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas. Consequently, more than 75% of the coal produced each year is simply burned in power plants to produce electricity. Methods to convert coal to gaseous fuels (*coal gasification*) or liquid fuels (*coal liquefaction*) exist, but are not particularly economical unless the prices of oil and natural gas are high. With the development of fracking and the subsequent fall in oil and natural gas prices interest in these processes has fallen however they have played an important role in the past. In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and $H_2$ known as *synthesis gas*, or *syngas*:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 5.8.1

$$C\,(s) + H_2O\,(g) \rightarrow CO\,(g) + H_2\,(g) \quad \Delta H = 131\ kJ \tag{5.8.1}$$

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases. Syngas or town gas was used for cooking until the 1960s when natural gas pipelines were built. Because syngas contains carbon monoxide (CO) it is poisonous, which accounts for scenes in old movies where people were killed by sticking their heads into an oven and allowing the gas to flow.

Syngas is can also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions:

$$\begin{array}{ll} 2C\,(s) + 2H_2O\,(g) \rightarrow \cancel{2CO\,(g)} + \cancel{2H_2\,(g)} & \Delta H_1 = 262\ kJ \\ \cancel{CO\,(g)} + \cancel{H_2O\,(g)} \rightarrow CO_2\,(g) + \cancel{H_2\,(g)} & \Delta H_2 = -41\ kJ \\ \cancel{CO\,(g)} + \cancel{3H_2\,(g)} \rightarrow CH_4\,(g) + \cancel{H_2O\,(g)} & \Delta H_3 = -206\ kJ \\ \hline 2C\,(s) + 2H_2O\,(g) \rightarrow CH_4\,(g) + CO_2\,(g) & \Delta H_3 = 15\ kJ \end{array} \tag{5.8.2}$$

Techniques available for converting coal to liquid fuels are not economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum.

## Petroleum

The petroleum that is pumped out of the ground is a complex mixture of several thousand organic compounds including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. The identities and relative abundences of the components vary depending on the source. So Texas crude oil is somewhat different from Saudi Arabian crude oil. In fact, the analysis of petroleum from different deposits can produce a "fingerprint" of each, which is useful in tracking down the sources of spilled crude oil. For example, Texas crude oil is "sweet," meaning that it contains a small amount of sulfur-containing molecules, whereas Saudi Arabian crude oil is "sour," meaning that it contains a relatively large amount of sulfur-containing molecules.

## Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Recall that distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure 5.8.5 shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in Figure 9.8.5 shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

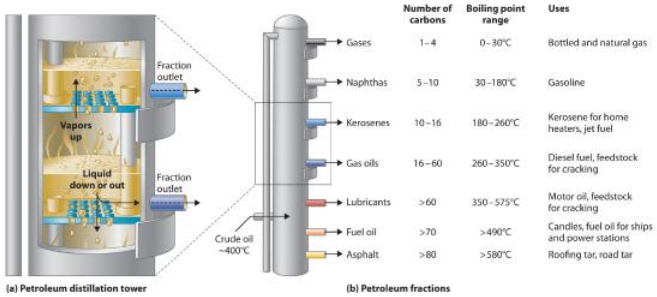



***Figure \(\PageIndex{5}\) : The Distillation of Petroleum.*** *(a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

The economics of petroleum refining are complex. For example, the market demand for kerosene and lubricants is much lower than the demand for gasoline, yet all three fractions are obtained from the distillation column in comparable amounts. Furthermore, most gasolines and jet fuels are blends with very carefully controlled compositions that cannot vary as their original feedstocks did. To make petroleum refining more profitable, the less volatile, lower-value fractions must be converted to more volatile, higher-value mixtures that have carefully controlled formulas. The first process used to accomplish this transformation is cracking, in which the larger and heavier hydrocarbons in the kerosene and higher-boiling-point fractions are heated to temperatures as high as 900°C. High-temperature reactions cause the carbon–carbon bonds to break, which converts the compounds to lighter molecules similar to those in the gasoline fraction. Thus in cracking, a straight-chain alkane with a number of carbon atoms corresponding to the kerosene fraction is converted to a mixture of hydrocarbons with a number of carbon atoms corresponding to the lighter gasoline fraction. The second process used to increase the amount of valuable products is called reforming; it is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons. Metal catalysts such as platinum are used to drive the necessary chemical reactions. The mixtures of products obtained from cracking and reforming are separated by fractional distillation.

## Octane Ratings

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 5.8.6 ), which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

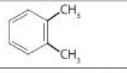
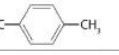
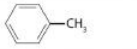
| Name | Condensed Structural Formula | Octane Rating | Name | Condensed Structural Formula | Octane Rating |
|---|---|---|---|---|---|
| *n*-heptane | $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ | 0 | *o*-xylene |  | 107 |
| *n*-hexane | $CH_3CH_2CH_2CH_2CH_2CH_3$ | 25 | ethanol | $CH_3CH_2OH$ | 108 |
| *n*-pentane | $CH_3CH_2CH_2CH_2CH_3$ | 62 | *t*-butyl alcohol | $(CH_3)_3COH$ | 113 |
| isooctane | $(CH_3)_3CCH_2CH(CH_3)_2$ | 100 | *p*-xylene |  | 116 |
| benzene |  | 106 | methyl *t*-butyl ether | $H_3COC(CH_3)_3$ | 116 |
| methanol | $CH_3OH$ | 107 | toluene |  | 118 |

Figure 5.8.6 *: The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

The octane scale was established in 1927 using a standard test engine and two pure compounds: n-heptane and isooctane (2,2,4-trimethylpentane). n-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89 \tag{5.8.3}$$

A gasoline that performs at the same level as a blend of 89% isooctane and 11% n-heptane is assigned an octane rating of 89; this represents an intermediate grade of gasoline. Regular gasoline typically has an octane rating of 87; premium has a rating of 93 or higher.

As shown in Figure 5.8.7, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead $[(C_2H_5)_4Pb]$, which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic.

Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place that combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

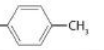
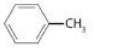
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| benzene |  | 106 | methyl *t*-butyl ether | $H_3COC(CH_3)_3$ | 116 |
| methanol | $CH_3OH$ | 107 | toluene |  | 118 |

Figure 5.8.7 *: The Octane Ratings of Some Hydrocarbons and Common Additives*

## Natural Gas

Natural gas is a (mostly) combustible gas found underground. While primarily composed of methane (70-90%) the gas from each well has a different composition and the value of the other components affects the value of the gas. The gas from wells that are rich in methane is called dry and wells that have a considerable amount of higher hydrocarbons produce wet gas. The higher hydrocarbons have value above that of methane so stripping them out is important. Some wells are sour because their gas has hydrogen sulfide which must be removed before the gas can be used for heating or generating electricity.

Finally, a few wells in Texas and nearby Oklahoma have a relatively high amount of helium (0.3 - 2.7%). The Helium Act of 1925 established a national helium reserve at Cliffside near Amarillo TX. Political pressure and costs pushed laws to privatize the reserve, but other policy considerations including the need for helium for scientific research has slowed the process.

**Table 5.8.4 : Composition of Natural Gas**

| Gas | Molecular Formula | Composition |
|---|---|---|
| Methane | $CH_4$ | 70-95% |
| Ethane | $C_2H_6$ | 0-20% |
| Carbon Dioxide | $CO_2$ | 0-8% |
| Nitrogen | $N_2$ | 0-5% |
| Hydrogen Sulfide | $H_2S$ | 0-5% |
| Propane | $C_3H_8$ | Traces |
| Butane | $C_4H_{10}$ | Traces |
| Rare Gases | He (also Ne) | 0-3% (only in Texas) |

The purification of natural gas is a complex process with many steps as each of the impurities is stripped out

Figure 5.8.8 **: Purification of natural gas:** *Prospective Chemical Engineers can find details about each process by searching the net. The flow chart is from the Wikipedia*

Gas turbine power plants to generate electricity are coming increasingly into use as fracking and other advanced drilling technologies have driven the cost of natural gas down and the supply up. While on a continental scale natural gas is transported by pipelines, natural gas can be cooled and compressed to be transported as liquified natural gas. Gas turbine power plants are small

and quickly built. They can be rapidly spun up to meet peak demand. More detailed information can be found at the Department of Energy Fossil Fuel web site

## The Carbon Cycle and the Greenhouse Effect

Since 1850 the burning of fossil fuels has increased the concentration of carbon dioxide in the atmosphere from 280 to just over 400 ppmV. A continued increase in the $CO_2$ burden in the atmosphere will have serious negative effects and this requires shifting our entire energy producing economy from fossil fuels to non-carbon sources such as hydro, solar, wind and nuclear. These include sea level rise that will threaten low lying cities including but not limited to Miami Beach and Norfolk in the US, even a meter or more coupled with storm surge and high tides can cause massive damage as was seen during Hurricane Sandy. Increased carbon dioxide in the atmosphere has already measurably decreased the pH of the oceans. Sea life is adapted to a narrow range of pH.

Higher global temperatures of 2 or 3 C may not seem much, but one should keep in mind that the average global temperature during the ice ages was only ~6 C lower than it is today. During the Eemian interglacial the average temperature was only a few degrees higher than the present and the sea level was 6-9 m higher. Finally, humans are mammals who maintain a core temperature within a few degrees of 37.0 C. In hot weather we do so by evaporation of sweat however there are limits to this and by 2100 there is a significant probability even in the US that at least a few days a year will reach this limit by 2100. Given that most people on earth do not have access to air conditioning, parts of the planet may become uninhabitable. Indeed a worst case and a serious problem that merits attention.

Given the constraints of this text it is difficult to provide the level of detail needed to understand why this is so. A good source for those interested in learning more is David Archer's Global Warming, Understanding the Forecast and An Introduction to Modern Climate Change by Andrew Dessler

There are a few basic facts that anyone starting to learn about the issue need to know. First, that the Earth gains energy from the Sun, and that it must radiate the energy at the same rate. If more energy is absorbed than radiated the Earth will warm up, if less energy is absorbed than radiated it will cool. Solar radiation follows a 5500 K blackbody distribution while radiation from the surface of the earth is also black body but at ~290K. This is shown schematically in Figure 5.8.9

> Figure 5.8.9 **: Origin of the greenhouse effect**. *The top box show the intensity of solar radiation at the top of the Earth's atmosphere to the left and the infrared emission from the atmosphere to the left. The next shows the net absorption in the atmosphere across the spectrum. The bottom show the absorption by different atmospheric species at their current concentrations. Figure from the Wikipedia*

The atmosphere cools with altitude up to about 15 km where it starts warming again because of absorption of UV radiation by ozone in the stratosphere. The transition between the troposphere and the stratosphere is called the tropopause and is the coldest part of the atmosphere.

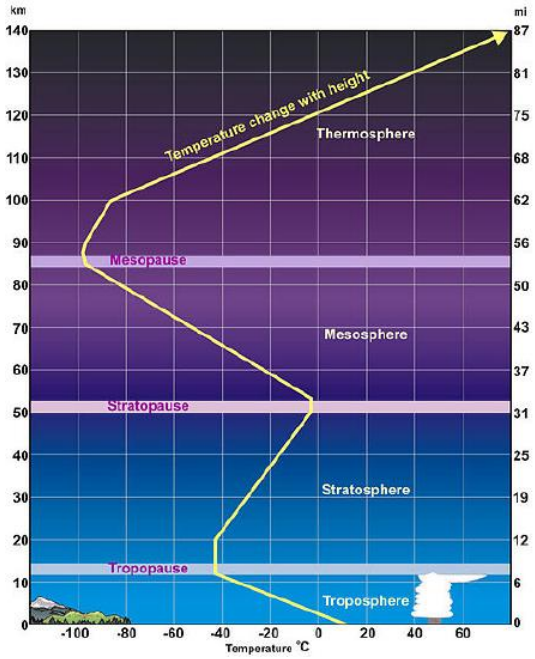



Figure 5.8.10 *The thermal structure of the atmosphere. The troposphere is the lowest level,extending from the the surface to the tropopause which is at 12-15 km altitude, more in the tropics and less less at the poles. The troposphere is the section of the atmosphere relevant to the greenhouse effect. The ozone layer is found in the stratosphere and one observes the aurora borealis or northern lights in the mesosphere Taken from Wikimedia*

Figure 5.8.11 shows the IR emission spectrum observed looking down on the earth from a high altitude balloon

Figure 5.8.11 **: High resolution far infrared emission spectrum of the atmosphere looking down from a high altitude balloon at 35 km.** *The strong band between 600 and 700 $cm^{-1}$ is associated with $CO_2$, the sharp band at ~ 1100 $cm^{-1}$ is associated with ozone and the feature near 1300 $cm^{-1}$ is due to methane. The sharp lines (the hair) are due to water vapor. Spectrum is from the Federal Earth Observation Portal and was taken by an instrument operated by NASA/Langeley Research Center*

The dotted lines in Figure 5.8.11 are blackbody curves. The IR window shown schematically in blue in Figure 5.8.9 is the region between the ozone and the carbon dioxide band, where the emission from the hot, 320 K ground follows the blackbody curve with a few sharp water vapor absorption lines. At those wavelengths, in the IR window, the emission comes directly from the surface. The $CO_2$ band extends down to about a 220 K blackbody curve. What this means is that radiation from $CO_2$ only escapes to space from the level in the troposphere where that is the temperature. The rate of emission is proportional to $T^4$ so the rate of emission from higher, therefore colder levels, is slower. Radiation in this area of the spectrum from the surface is blocked and only the greatly reduced emission from the upper troposphere escapes to space. The same is true for the ozone and methane bands as well as the water lines.

The net effect is that the surface must warm in order to maintain the balance between incoming solar radiation and the outgoing emission. There is a simple calculation which models the atmosphere as a one dimensional problem and calculates what the temperature of the surface would be if there were no greenhouse gases. The result is 255 K, rather cold. In fact if one attempts a more complex calculation the effective temperature without greenhouse gases would be even colder.

What happens if we increase the carbon dioxide in the atmosphere? The altitude at which the atmosphere can emit radiation to space will rise because of increased absorption by the $CO_2$. Since in the troposphere the temperature decreases with altitude, the rate of emission from a higher level must decrease. Again, in order to maintain the balance between incoming solar radiation and the outgoing emission the surface will have to warm even more, thus the term global warming. The change is not linear with increasing $CO_2$ but logarithmic. But, of course it is not so simple, because increasing the surface temperature will increase the water vapor pressure in the atmosphere, which will increase the temperature further.

We also have to understand the flow of carbon between the atmosphere, the biosphere, the upper oceans and the deep. Observations to date show that natural emissions of $CO_2$ from these reservoirs are in balance with absorption, while only about half of fossil fuel emissions remain in the atmosphere, the rest being absorbed by the upper ocean and the biosphere. The three upper reservoirs equilibrate in a decade or less, but flow into the deep ocean requires roughly a thousand years.

Figure from the Wikipedia

There is no doubt that atmospheric $CO_2$ levels are increasing, and the major reason for this increase is the combustion of fossil fuels. An extremely conservative statement of the situation today can be found in the 2014 Synthesis Report from the IPCC, a consensus between scientists and policymakers. The report starkly states that

> Cumulative emissions of $CO_2$ largely determine global mean surface warming by the late 21st century and beyond.

and concludes that

> Continued emission of greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive and irreversible impacts for people and ecosystems. Limiting climate change would require substantial and sustained reductions in greenhouse gas emissions which, together with adaptation, can limit climate change risks.

The situation is serious, but we can work together to limit and even reverse damage while maintaining our standard of living in the developed world while helping the developing world to a better future. However, the issues are complex and we can only touch on some of the basics here.

## Summary

More than 80% of the energy used by modern society (about $3 \times 10^{17}$ kJ/yr) is from the combustion of fossil fuels. Because of their availability, ease of transport, and facile conversion to convenient fuels, natural gas and petroleum are currently the preferred fuels. Coal is primarily used for electricity generation. The combustion of fossil fuels releases large amounts of $CO_2$ that upset the balance of the **carbon cycle** and result in a steady increase in atmospheric $CO_2$ levels. Because $CO_2$ is a **greenhouse gas**, which absorbs heat before it can be radiated from Earth into space, $CO_2$ in the atmosphere results in increased surface temperatures (the **greenhouse effect**).

## Key Takeaway

- Thermochemical concepts can be used to calculate the efficiency of various forms of fuel, which can then be applied to environmental issues.

## Conceptual Problems

1. What is meant by the term *greenhouse gases*? List three greenhouse gases that have been implicated in global warming.
2. Name three factors that determine the rate of planetary $CO_2$ uptake.
3. The structure of coal is quite different from the structure of gasoline. How do their structural differences affect their enthalpies of combustion? Explain your answer.

## Numerical Problems

1. One of the side reactions that occurs during the burning of fossil fuels is

   $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

   1. How many kilojoules of energy are released during the combustion of 10 lb of $FeS_2$?
   2. How many pounds of $SO_2$ are released into the atmosphere?
   3. Discuss the potential environmental impacts of this combustion reaction.
2. How many kilograms of $CO_2$ are released during the combustion of 16 gal of gasoline? Assume that gasoline is pure isooctane with a density of 0.6919 g/mL. If this combustion was used to heat $4.5 \times 10^3$ L of water from an initial temperature of 11.0°C, what would be the final temperature of the water assuming 42% efficiency in the energy transfer?
3. A 60 W light bulb is burned for 6 hours. If we assume an efficiency of 38% in the conversion of energy from oil to electricity, how much oil must be consumed to supply the electrical energy needed to light the bulb? (1 W = 1 J/s)
4. How many liters of cyclohexane must be burned to release as much energy as burning 10.0 lb of pine logs? The density of cyclohexane is 0.7785 g/mL, and its $\Delta H_{comb} = -46.6$ kJ/g.

## Contributors

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Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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# 5.9: Essential Skills 4

**Learning Objectives**

- Temperature
- Unit Conversions: Dimensional Analysis

The previous Essential Skills sections introduced some fundamental operations that you need to successfully manipulate mathematical equations in chemistry. This section describes how to convert between temperature scales and further develops the topic of unit conversions started in Essential Skills 2 .

## Temperature

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures.

Science only uses SI and derived units with few if any exceptions. Therefore this text avoids conversions between customary units (foot, pound, Farenheit) that are simply inappropriate and only used in a few countries.

Two different scales are commonly used to measure temperature: Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

## The Celsius Scale

The Celsius scale was developed in 1742 by the Swedish astronomer Anders Celsius. It is based on the melting and boiling points of water under normal atmospheric conditions. The current scale is an inverted form of the original scale, which was divided into 100 increments. Because of these 100 divisions, the Celsius scale is also called the *centigrade scale*.

## The Kelvin Scale

Lord Kelvin, working in Scotland, developed the Kelvin scale in 1848. His scale uses molecular energy to define the extremes of hot and cold. Absolute zero, or 0 K, corresponds to the point at which molecular energy is at a minimum. The Kelvin scale is preferred in scientific work, although the Celsius scale is also commonly used. Temperatures measured on the Kelvin scale are reported simply as K, not °K.

## Converting between Scales

The kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K. The Kelvin and Celsius scales are related as follows:

$$T\,(in^oC) + 273.15 = T\,(in\ K) \tag{5.9.1}$$

$$T\,(in\ K) - 273.15 = T\,(in^oC) \tag{5.9.2}$$

### Skill Builder ES1

1. Convert the temperature of the surface of the sun (5800 K) and the boiling points of gold (3080 K) and liquid nitrogen (77.36 K) to °C .

**Solution:**

1. Sun: 5800 K = (5800 -273.15) $^oC$ = 5527 $^oC$

Liquid Gold: 3080 K = (3080 -273.15) $^oC$ =2807 $^oC$

Liquid $N_2$ 77.36 K = (77.36 -274.15) $^oC$ = -195.79 $^oC$

## Unit Conversions: Dimensional Analysis

In Essential Skills 2, you learned a convenient way of converting between units of measure, such as from grams to kilograms or seconds to hours. The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*. For example, if we observe experimentally that an object's potential energy is related to its mass, its height from the ground, and to a gravitational force, then when multiplied, the units of mass, height, and the force of gravity must give us units corresponding to those of energy.

Energy is typically measured in joules, calories, or electron volts (eV), defined by the following expressions:

$$1\ J = 1\ \left(kg \cdot m^2\right)/s^2 = 1\ coulomb \cdot volt \tag{5.9.3}$$

$$1\ cal = 4.184\ J \tag{5.9.4}$$

$$1eV = 1.602 \times 10^{-19} J \tag{5.9.5}$$

To illustrate the use of dimensional analysis to solve energy problems, let us calculate the kinetic energy in joules of a 320 g object traveling at 123 cm/s. To obtain an answer in joules, we must convert grams to kilograms and centimeters to meters. Using Equation 5.1.5, the calculation may be set up as follows:

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}\,(g)\left[\left(\frac{cm}{s}\right)\left(\frac{cm}{s}\right)\right]^2 \tag{5.9.6}$$

$$= \left(\cancel{g}\right)\left(\frac{kg}{\cancel{g}}\right)\left(\frac{\cancel{cm^2}}{s^2}\right)\left(\frac{m^2}{\cancel{cm^2}}\right) = \frac{kg \cdot m^2}{s^2} \tag{5.9.7}$$

$$= \frac{1}{2}320\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left[\left(\frac{123\ \cancel{cm}}{1\ s}\right)\left(\frac{1\ m}{100\ \cancel{cm}}\right)\right]^2 = \frac{0.320\ kg}{2}\left[\frac{123\ m}{s\,(100)}\right]^2 \tag{5.9.8}$$

$$= 0.242\ kg \cdot m^2/s^2 = 0.242\ J \tag{5.9.9}$$

Alternatively, the conversions may be carried out in a stepwise manner:

$$320\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right) = 0.320\ kg \tag{5.9.10}$$

$$123\ \cancel{cm}\left(\frac{1\ m}{100\ \cancel{cm}}\right) = 1.23\ m \tag{5.9.11}$$

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}\,(g)\left[\left(\frac{cm}{s}\right)\left(\frac{cm}{s}\right)\right]^2 \tag{5.9.12}$$

$$KE = \frac{1}{2}\,(0.320kg)\left(\frac{1.23\ m}{s}\right)^2 = 0.242\left(kg \cdot m^2/s^2\right) = 0.242\ J \tag{5.9.13}$$

However, this second method involves an additional step

A small discrepancy between answers using the different methods might be expected due to rounding to the correct number of significant figures for each step when carrying out the calculation in a stepwise manner. Recall that all digits in the calculator should be carried forward when carrying out a calculation using multiple steps. In this problem, we first converted kilocalories to kilojoules and then converted ounces to grams. Skill Builder ES2 allows you to practice making multiple conversions between units in a single step.

### Skill Builder ES2

1. Write a single equation to show how to convert cm/min to km/h; °C/s to K/h.

**Solution:**

1. $$\left[\left(\frac{\cancel{cm}}{\cancel{min}}\right)\left(\frac{1\ \cancel{m}}{100\ \cancel{cm}}\right)\left(\frac{1\ km}{1000\ \cancel{m}}\right)\left(\frac{60\ \cancel{min}}{1\ h}\right) = km/h \tag{5.9.14}$$

$$\left(\frac{^{o}C}{\cancel{s}}\right)\left(\frac{60\ \cancel{s}}{1\ \cancel{min}}\right)\left(\frac{60\ \cancel{min}}{h}\right)+273.15\ K=K/h \tag{5.9.15}$$

## Contributors

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Modified by Joshua Halpern

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# CHAPTER OVERVIEW

## 6: The Structure of Atoms


6.1: Waves and Electromagnetic Radiation
6.2: Quantization of Energy
6.3: Atomic Spectra and Models of the Atom
6.4: Wave - Particle Duality
6.5: Atomic Orbitals and Their Energies
6.6: Building Up The Periodic Table
6.7: Electronic Structure of the Transition Metals



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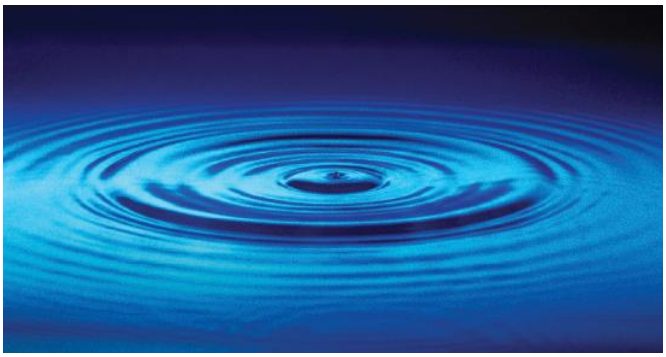
# 6.1: Waves and Electromagnetic Radiation

**Learning Objectives**

- To learn about the characteristics of electromagnetic waves.
- Types include light, X-Rays, infrared and microwaves

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.

**Figure 2.1.1 A Wave in Water**

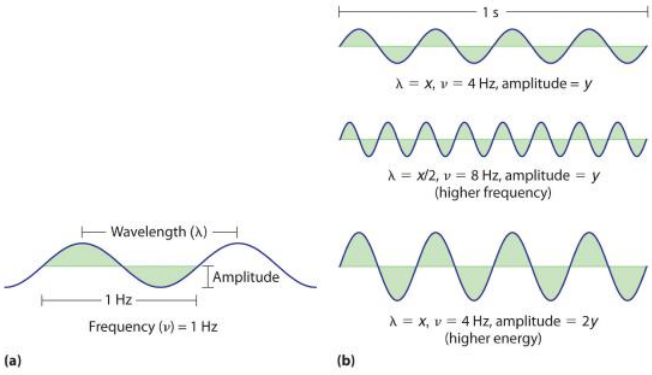


*When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.*

## Properties of Waves

A wave A periodic oscillation that transmits energy through space. is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 2.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

**Figure 2.1.2 Important Properties of Waves**




*(a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.*

Waves have characteristic properties (Figure 2.1.2). As you may have noticed in Figure 2.1.1, waves are periodicPhenomena, such as waves, that repeat regularly in both space and time.; that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ)The distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs.. λ is the lowercase Greek lambda, and ν is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν)The number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second (1/s = $s^{-1}$), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation. The amplitudeThe vertical height of a wave, which is defined as half the peak-to-trough height., or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 2.1.2 , two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (*v*)The distance traveled by a wave per unit time., which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(wavelength)(frequency) = speed$$

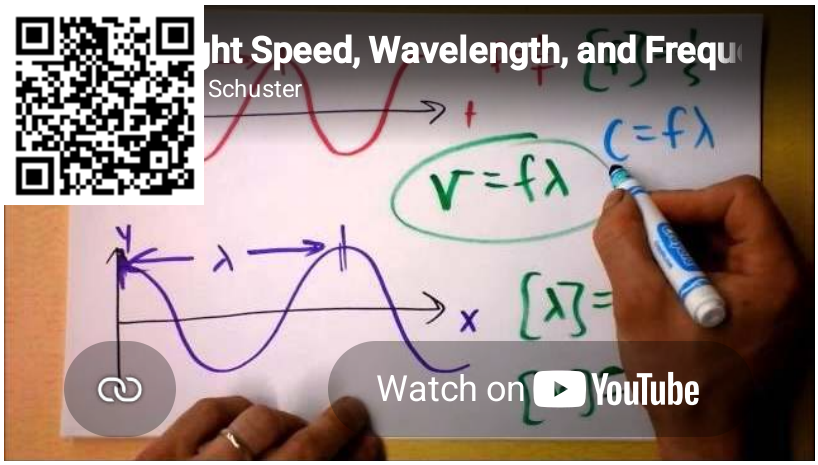
$$\lambda\nu = v$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second}$$

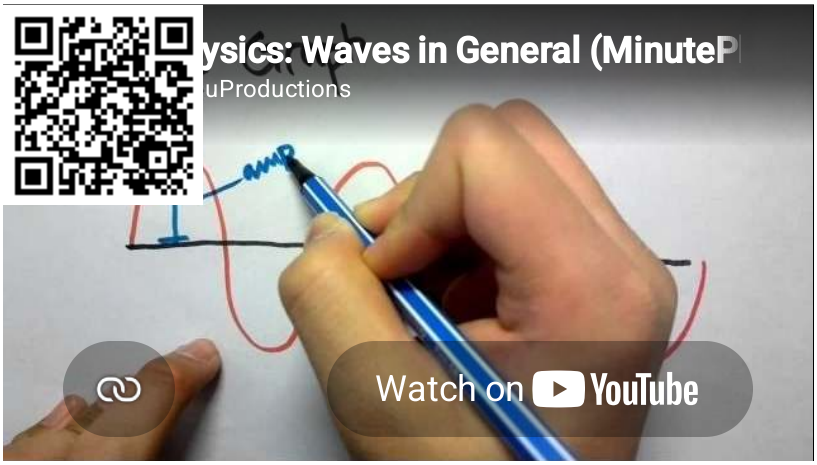
Be careful not to confuse the symbols for the speed, *v*, with the frequency, *ν*.

Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

## Videos




Light Speed, Wavelength, and Frequency | Dimensional Analysis by Doc Schuster




Waves in General by JaHu Productions - a bit faster. Also discusses sound waves

## Electromagnetic Radiation

**Figure 2.1.3 The Nature of Electromagnetic Radiation**

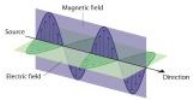


Figure 2.1.3 The Nature of Electromagnetic **Radiation** *All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.*

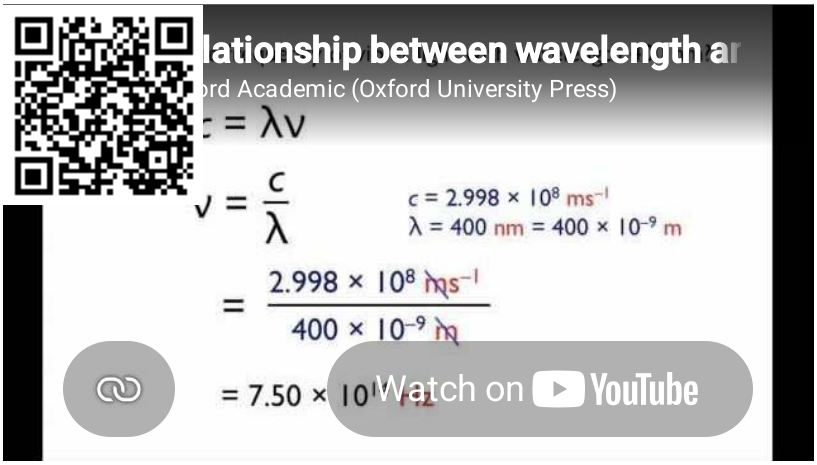
Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation Energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 2.1.3). Some forms of electromagnetic radiation are shown in Figure 2.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (*c*)The speed with which all forms of electromagnetic radiation travel in a vacuum., a fundamental physical constant with a value of 2.99792458 × $10^8$ m/s (which is about 3.00 ×$10^8$ m/s or 1.86 × $10^5$ mi/s). This is about a million times faster than the speed of sound.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure 2.1.4 and Table 2.1.1 , the wavelengths of familiar electromagnetic radiation range from $10^1$ m for radio waves to $10^{-12}$ m for gamma rays, which are emitted by nuclear reactions. By replacing *v* with *c* in Equation 2.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda\nu$$
$$\nu = \frac{c}{\lambda}$$

For example, the frequency of radio waves is about $10^8$ Hz, whereas the frequency of gamma rays is about $10^{20}$ Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7 × $10^{-7}$ m (700 nm, or 4.3 × $10^{14}$ Hz) and 4 × $10^{-7}$ m (400 nm, or 7.5 × $10^{14}$ Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly when frequency decreases, wavelength increases,

Here is a video from Oxford University Press which goes through the calculation




## Videos

- Calculating Frequency Given Wavelength - Johnny Cantrell
- .Wavelength Frequency Problems - Cayer Chem

## Examples

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

Within this visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 2.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

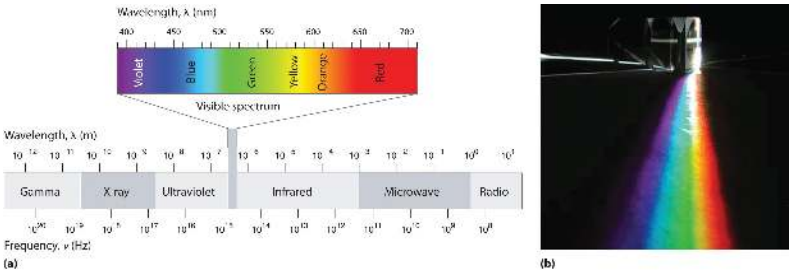



Figure 2.1.4 The Electromagnetic Spectrum *(a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.*

This video reviews the ideas in Figure 2.1.4

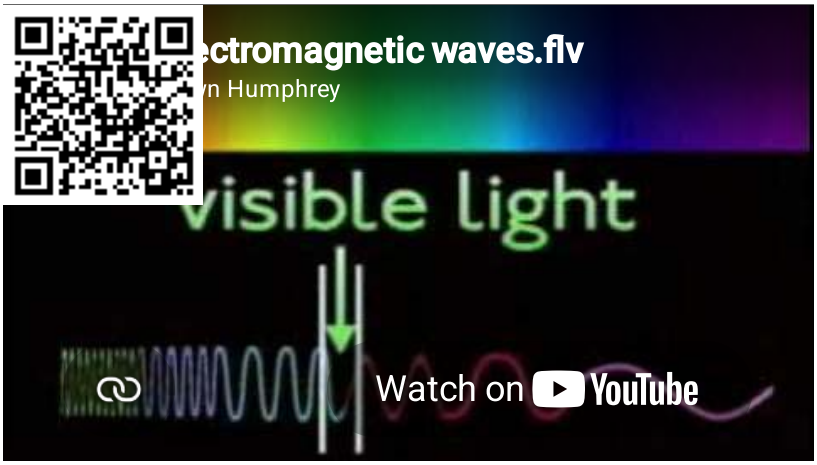



**Table 2.1.1 Common Wavelength Units for Electromagnetic Radiation**

| Unit | Symbol | Wavelength (m) | Type of Radiation |
|---|---|---|---|
| picometer | pm | $10^{-12}$ | gamma ray |
| angstrom | Å | $10^{-10}$ | x-ray |
| nanometer | nm | $10^{-9}$ | x-ray |
| micrometer | µm | $10^{-6}$ | infrared |
| millimeter | mm | $10^{-3}$ | infrared |
| centimeter | cm | $10^{-2}$ | microwave |
| meter | m | $10^{0}$ | radio |

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu$$

$$E \propto \frac{1}{\lambda}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer described in Chapter 7.6 "Chemical Reactions in the Atmosphere" absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

### Note the Pattern

The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.

### Example 2.1.1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

**Given:** frequency

**Asked for:** wavelength

**Strategy:**

Substitute the value for the speed of light in meters per second into Equation 2.1.2 to calculate the wavelength in meters.

**Solution:**

From Equation 2.1.2 , we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998 × $10^8$ m/s:

$$\lambda\nu = c = 2.998 \times 10^8 m/s$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu} = \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) = 2.965\ m$$

Exercise

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

**Answer:** 8.45 mm

In Section 2.2 and Section 2.3, we describe how scientists developed our current understanding of the structure of atoms using the scientific method described in Chapter 1. You will discover why scientists had to rethink their classical understanding of the nature of electromagnetic energy, which clearly distinguished between the particulate behavior of matter and the wavelike nature of energy.

## Key Equations

**relationship between wavelength, frequency, and speed of a wave**

Equation 2.1.1: $v = \lambda\nu$

**relationship between wavelength, frequency, and speed of electromagnetic radiation**

Equation 2.1.2: $c = \lambda\nu$

## Summary

A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength (λ)**, the distance between successive waves; **frequency (ν)**, the number of waves that pass a fixed point per unit time; **speed (*v*)**, the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light (*c*)**. Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ only in their frequencies and wavelengths.

## Key Takeaway

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

## Conceptual Problems

1. What are the characteristics of a wave? What is the relationship between electromagnetic radiation and wave energy?
2. At constant wavelength, what effect does increasing the frequency of a wave have on its speed? its amplitude?
3. List the following forms of electromagnetic radiation in order of increasing wavelength: x-rays, radio waves, infrared waves, microwaves, ultraviolet waves, visible waves, and gamma rays. List them in order of increasing frequency. Which has the highest energy?
4. A large industry is centered on developing skin-care products, such as suntan lotions and cosmetics, that cannot be penetrated by ultraviolet radiation. How does the wavelength of visible light compare with the wavelength of ultraviolet light? How does the energy of visible light compare with the energy of ultraviolet light? Why is this industry focused on blocking ultraviolet light rather than visible light?

## Numerical Problems

1. The human eye is sensitive to what fraction of the electromagnetic spectrum, assuming a typical spectral range of $10^4$ to $10^{20}$ Hz? If we came from the planet Krypton and had x-ray vision (i.e., if our eyes were sensitive to x-rays in addition to visible light), how would this fraction be changed?
2. What is the frequency in megahertz corresponding to each wavelength?
    1. 755 m
    2. 6.73 nm
    3. $1.77 \times 10^3$ km
    4. 9.88 Å
    5. $3.7 \times 10^{-10}$ m
3. What is the frequency in megahertz corresponding to each wavelength?
    1. $5.8 \times 10^{-7}$ m
    2. 2.3 Å
    3. $8.6 \times 10^7$ m
    4. 6.2 mm
    5. 3.7 nm
4. Line spectra are also observed for molecular species. Given the following characteristic wavelengths for each species, identify the spectral region (ultraviolet, visible, etc.) in which the following line spectra will occur. Given 1.00 mol of each compound and the wavelength of absorbed or emitted light, how much energy does this correspond to?
    1. $NH_3$, $1.0 \times 10^{-2}$ m
    2. $CH_3CH_2OH$, 9.0 μm
    3. Mo atom, 7.1 Å
5. What is the speed of a wave in meters per second that has a wavelength of 1250 m and a frequency of $2.36 \times 10^5$ $s^{-1}$?
6. A wave travels at 3.70 m/s with a frequency of $4.599 \times 10^7$ Hz and an amplitude of 1.0 m. What is its wavelength in nanometers?
7. An AM radio station broadcasts with a wavelength of 248.0 m. What is the broadcast frequency of the station in kilohertz? An AM station has a broadcast range of 92.6 MHz. What is the corresponding wavelength range in meters for this reception?
8. An FM radio station broadcasts with a wavelength of 3.21 m. What is the broadcast frequency of the station in megahertz? An FM radio typically has a broadcast range of 82–112 MHz. What is the corresponding wavelength range in meters for this reception?
9. A microwave oven operates at a frequency of approximately 2450 MHz. What is the corresponding wavelength? Water, with its polar molecules, absorbs electromagnetic radiation primarily in the infrared portion of the spectrum. Given this fact, why are microwave ovens used for cooking food?

## Contributors

- Anonymous

Modified by Joshua Halpern

Light Speed Video from Doc Schuster on YouTube

Wave Video from JaHuProductions on YouTube

Wavelength and Frequency from Oxford Academic on YouTube

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# 6.2: Quantization of Energy

**Learning Objectives**

- To understand how energy is quantized

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

## Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation. Electromagnetic radiation whose wavelength and color depends on the temperature of the object., the energy emitted by an object when it is heated. The wavelength of energy emitted by an object depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light (Figure 2.2.1).



Figure 2.2.1 Blackbody Radiation *When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as an electric stove element, on a low setting appears red, whereas a higher-temperature object, such as the filament of an incandescent light bulb, appears yellow or white.*

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure 2.2.2. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 2.2.2 . Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 2.2.2, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum..

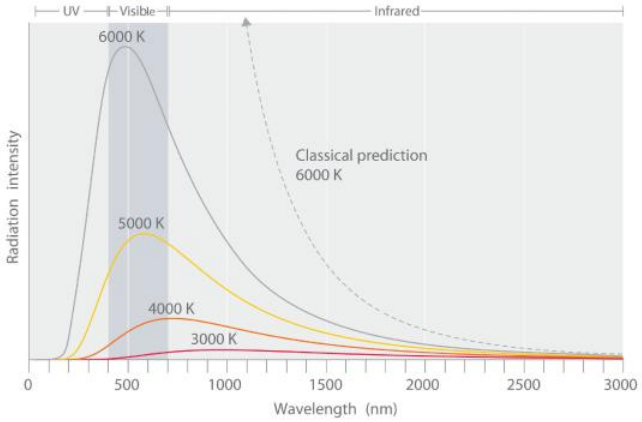



Figure 2.2.2 Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It **Emits** *At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 2.2.1 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure 2.14). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.*

## Max Planck (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government. One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of −1 or −2 but *not* −1.33 electron charges.

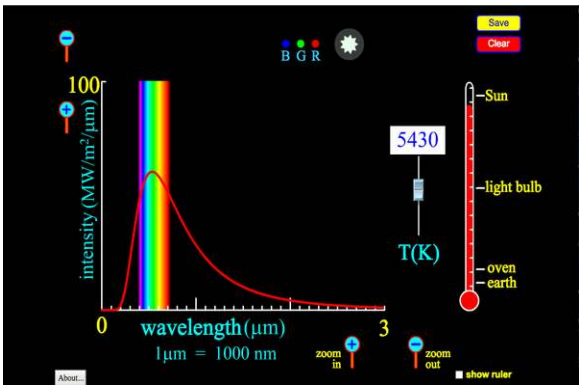
Planck postulated that the energy of a particular quantum of radiant energy could be described explicitly by the equation

$$E = h\nu \tag{2.2.1}$$

where the proportionality constant $h$ is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34}\ J \cdot s(\text{joule-seconds}) \tag{6.2.1}$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of *h*ν, Planck devised an equation that fit the experimental data shown in Figure 2.2.2. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 2.2.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature. You can get a feel for this by clicking on the black body applet from PHeT below. (you may need to install JAVA to run the applets).




At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

### Videos

- Calculating Energy of a Mole of Photons - Johnny Cantrell
- .Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.

### Examples

Same as before

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

## The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 2.2.3 ). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (a phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

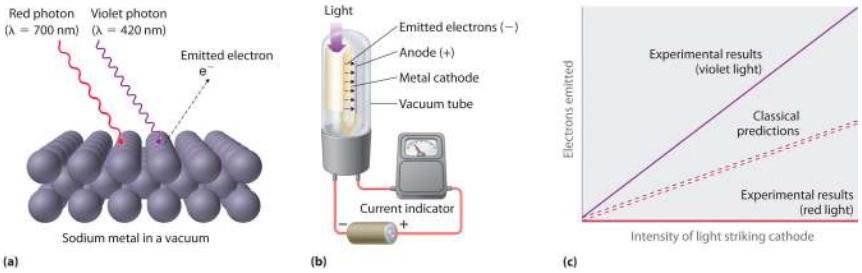
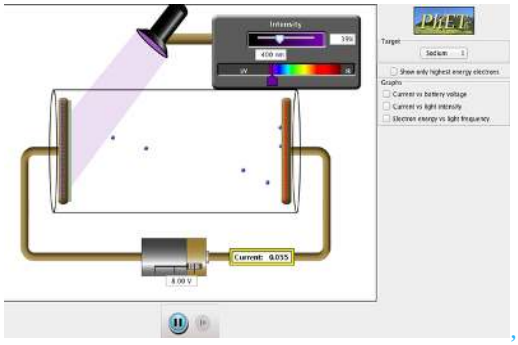



Figure 2.2.3 The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than $E_o$, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.*

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call photons. Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = h\nu_o$). If photons of light with energy less than $E_o$ strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than $E_o$ strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

$$kinetic\ energy\ of\ ejected\ electron = E - E_o = h\nu - h\nu_o = h\,(\nu - \nu_o) \tag{2.2.2}$$

When a metal is struck by light with energy above the threshold energy $E_o$, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics. KCVS has an applet which illustrates the photoelectric effect and here is another from PHET which you can run by clicking on (it also requires JAVA)




## Albert Einstein (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics. In 1905, his "miracle year" he published four papers that revolutionized physics. One was on the special theory of relativity, a second on the equivalence of mass and energy, a third on Brownian motion, and the fourth on the photoelectric effect, for which he received the Nobel Prize in 1921, the theory of relativity and energy-matter equivalence being still controversial at the time

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms.

### Example 2.2.1

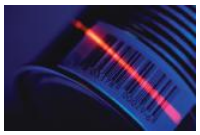


Figure 2.2.4 A Beam of Red Light Emitted by a Helium Neon laser reads a bar **code** *Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.*

A ruby laser, a device that produces light in a narrow range of wavelengths (Section 2.3), emits red light at a wavelength of 694.3 nm (Figure 6.8 ). What is the energy in joules of a single photon?

**Given:** wavelength

**Asked for:** energy of single photon.

**Strategy:**

**A** Use Equation 2.1.1 and Equation 2.2.1 to calculate the energy in joules.

**Solution:**

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

Exercise

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

1. What is the energy in joules of a single photon?
2. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

**Answer**

1. $1.287 \times 10^{-15}$ J/photon
2. 4497 times

## Key Equation

**quantization of energy** $E = h\nu$

## Summary

The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant *h* is a fundamental constant (Planck's constant). Albert Einstein used Planck's concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = h\nu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

## Key Takeaway

- The fundamental building blocks of energy are quanta and of matter are atoms.

## Conceptual Problems

1. Describe the relationship between the energy of a photon and its frequency.
2. How was the ultraviolet catastrophe explained?
3. If electromagnetic radiation with a continuous range of frequencies above the threshold frequency of a metal is allowed to strike a metal surface, is the kinetic energy of the ejected electrons continuous or quantized? Explain your answer.
4. The vibrational energy of a plucked guitar string is said to be *quantized*. What do we mean by this? Are the sounds emitted from the 88 keys on a piano also quantized?

5. Which of the following exhibit quantized behavior: a human voice, the speed of a car, a harp, the colors of light, automobile tire sizes, waves from a speedboat?

## Answers

1. The energy of a photon is directly proportional to the frequency of the electromagnetic radiation.
2. 
3. 
4. 
5. Quantized: harp, tire size, speedboat waves; continuous: human voice, colors of light, car speed.

## Numerical Problems

1. What is the energy of a photon of light with each wavelength? To which region of the electromagnetic spectrum does each wavelength belong?
    1. $4.33 \times 10^5$ m
    2. 0.065 nm
    3. 786 pm
2. How much energy is contained in each of the following? To which region of the electromagnetic spectrum does each wavelength belong?
    1. 250 photons with a wavelength of 3.0 m
    2. $4.2 \times 10^6$ photons with a wavelength of 92 μm
    3. $1.78 \times 10^{22}$ photons with a wavelength of 2.1 Å
3. A 6.023 x $10^{23}$ photons are found to have an energy of 225 kJ. What is the wavelength of the radiation?
4. Use the data in Table 2.1.1 to calculate how much more energetic a single gamma-ray photon is than a radio-wave photon. How many photons from a radio source operating at a frequency of $8 \times 10^5$ Hz would be required to provide the same amount of energy as a single gamma-ray photon with a frequency of $3 \times 10^{19}$ Hz?
5. Use the data in Table 2.1.1 to calculate how much more energetic a single x-ray photon is than a photon of ultraviolet light.
6. A radio station has a transmitter that broadcasts at a frequency of 100.7 MHz with a power output of 50 kW. Given that 1 W = 1 J/s, how many photons are emitted by the transmitter each second?

## Answers

1. 
    1. $4.59 \times 10^{-31}$ J/photon, radio
    2. $3.1 \times 10^{-15}$ J/photon, gamma ray
    3. $2.53 \times 10^{-16}$ J/photon, gamma ray
2. 
3. 532 nm
4. 
5. 
6. 

## Contributors

- Anonymous

Modified by Joshua Halpern (Howard University)

Blackbody Radiation Applet from pHet

Photoelectric Effect Applet from pHet

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# 6.3: Atomic Spectra and Models of the Atom

**Learning Objectives**

- To learn about the relationship between atomic spectra and the electronic structure of atoms

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation. In this section, we describe how experimentation with visible light provided this evidence.

## Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation (Figure 2.2.2), a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of $H_2$ emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines, called a line spectrum. A spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths., are seen (Figure 2.3.1 ), rather than a continuous range of colors. The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

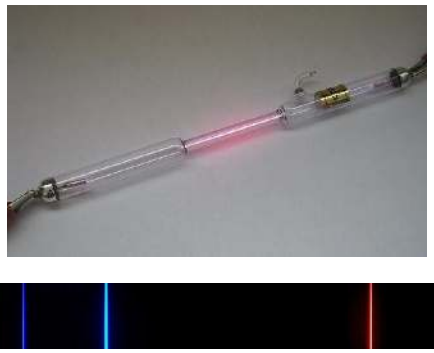


Figure 2.3.1 The Emission of Light by Hydrogen Atoms *(a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.*

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation (Equation 2..2.1): the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of *E* were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$\nu = constant\ \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where *n* = 3, 4, 5, 6. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \Re \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where $n_1$ and $n_2$ are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of $1.09737 \times 10^7\ m^{-1}$.

### Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous. He published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with $n_1 = 2$, $n_2 = 3, 4, 5,\ldots$). More important, Rydberg's equation also described the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_1 = 1$, $n_2 = 2, 3, 4,\ldots$) and one in the infrared ($n_1 = 3$, $n_2 = 4, 5, 6$). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

### Videos

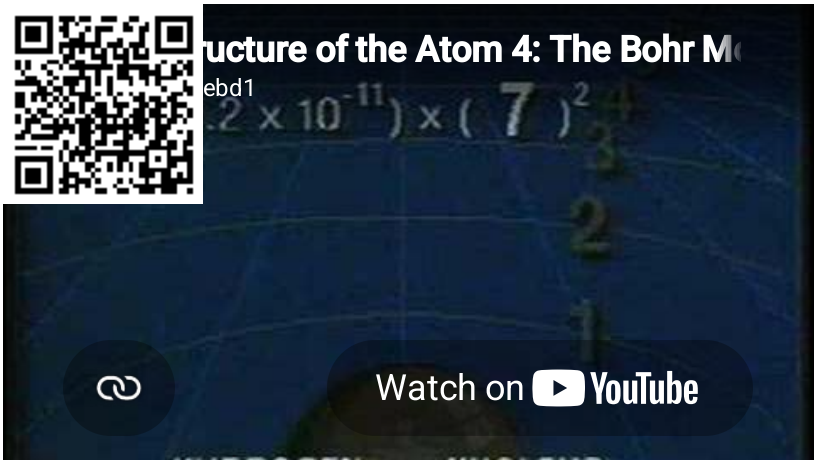
- Demonstration of the Balmer series spectrum - Mike Jones
- Bohr's Model Problems - Chemistry Solution
- Bohr Model of H - Jchorton

### Examples

- Quantum Chemistry - Ohio State
- Bohr Atom Energy Levels and Bohr Atom Energy Change - About Education
- Bohr Model Quiz - Thurston High School

## The Bohr Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* As discussed in Chapter 1, Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.




### Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project. In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

Using classical physics, Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\Re hc}{n^2} \tag{2.3.3}$$

where $\Re$ is the Rydberg constant, $h$ is Planck's constant, $c$ is the speed of light, and $n$ is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.

As $n$ decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with $n = 1$ is the lowest lying and most tightly bound. The negative sign in Equation 2.3.3 indicates that the electron-nucleus pair is more tightly bound when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the ground state. The most stable arrangement of electrons for an element or a compound., the most stable arrangement for a hydrogen atom. As $n$ increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 2.10 ). A hydrogen atom with an electron in an orbit with $n > 1$ is therefore in an excited state. Any arrangement of electrons that is higher in energy than the ground state.: its energy is higher than the energy of the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called *decay*, it loses energy by emitting a photon whose energy corresponds to the difference in energy between the two states (Figure 2.3.1 ).

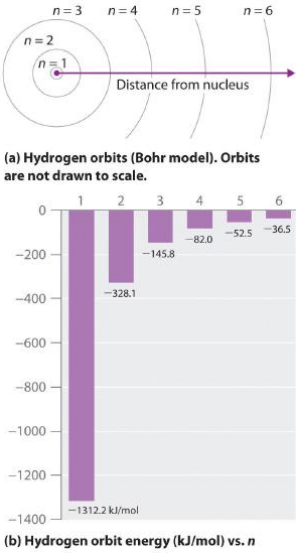



Figure 2.3.2 The Bohr Model of the Hydrogen Atom *(a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.*

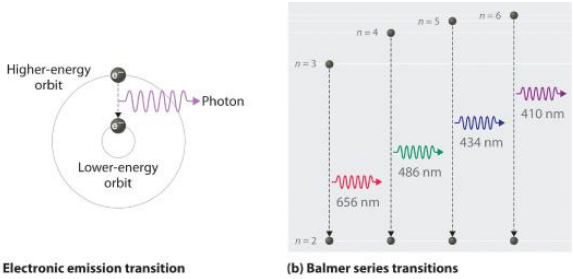



Figure 2.3.3 The Emission of Light by a Hydrogen Atom in an Excited State *(a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with n ≥ 3 to the orbit with n = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.*

So the difference in energy ($\Delta E$) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where $n_1$ is the final orbit and $n_2$ the initial orbit. Substituting from Bohr's equation (Equation 2.9) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{2.3.4}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 2.11 . Substituting $hc/\lambda$ for $\Delta E$ gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation 2.11 and Equation 2.12 indicates that energy is released as the electron moves from orbit $n_2$ to orbit $n_1$ because orbit $n_2$ is at a higher energy than orbit $n_1$. Bohr calculated the value of <math xml:id="av_1.0-ch02_m019" display="inline"><semantics><mi>ℜ</mi></semantics></math> from fundamental constants such as the charge and mass of the electron and Planck's constate and obtained a value of $1.0974 \times 10^7\ m^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (part (b) in Figure 2.9 ). As shown in part (b) in Figure 2.11 , the lines in this series correspond to transitions from higher-energy orbits ($n > 2$) to the *second* orbit ($n = 2$). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state ($n > 2$) to a lower-energy state ($n = 2$) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the *difference* in energy between the two states (part (a) in Figure 2.11 ). The $n = 3$ to $n = 2$ transition gives rise to the line at 656 nm (red), the $n = 4$ to $n = 2$ transition to the line at 486 nm (green), the $n = 5$ to $n = 2$ transition to the line at 434 nm (blue), and the $n = 6$ to $n = 2$ transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the $n = 3$ than the $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic red color of a hydrogen discharge (part (a) in Figure 2.3.1 ). Other families of lines are produced by transitions from excited states with $n > 1$ to the orbit with $n = 1$ or to orbits with $n \geq 3$. These transitions are shown schematically in Figure 2.3.4

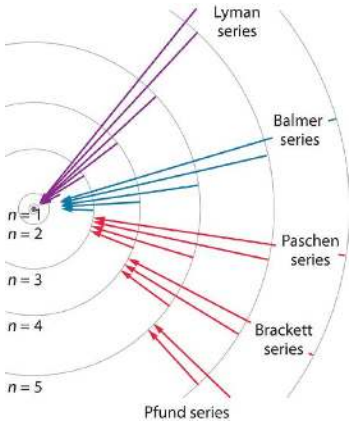



Figure 2.3.4 Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen *The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)*

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis. To achieve the accuracy required for modern purposes, physicists have turned to the

atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum. In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

### Example 2.3.1

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the $n$ = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

**Given:** lowest-energy orbit in the Lyman series

**Asked for:** wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

**Strategy:**

**A** Substitute the appropriate values into Equation 2.3.2 (the Rydberg equation) and solve for λ.

**B** Use Figure 2.1.4 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

**Solution:**

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

**A** For the Lyman series, $n_1$ = 1. The lowest-energy line is due to a transition from the $n$ = 2 to $n$ = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1}$$

It turns out that spectroscopists (the people who study spectroscopy) use $cm^{-1}$ rather than $m^{-1}$ as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, $E=h\nu$. Spectroscopists often talk about energy and frequency as equivalent. The $cm^{-1}$ unit is particularly convenient. The infrared range is roughy 200 - 5,000 $cm^{-1}$, the visible from 11,000 to 25.000 $cm^{-1}$ and the UV between 25,000 and 100,000 $cm^{-1}$. The units of $cm^{-1}$ are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to $cm^{-1}$.

$$\varpi = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m^{-1}}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1}$$

and

$$\lambda = 1.215 \times 10^{-7}\ \text{m} = 122\ \text{nm}$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating $O_2$ molecules to O atoms which react with other $O_2$ molecules to form stratospheric ozone

**B** This wavelength is in the ultraviolet region of the spectrum.

Exercise

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n$ = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

**Answer:** $4.65 \times 10^3$ nm; infrared

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 2.3.5 ). In fact, Bohr's model worked only for species that contained just one electron: H, $He^{+}$, $Li^{2+}$, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

Figure 2.3.5 The Emission Spectra of Elements Compared with Hydrogen *These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.*

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrumA spectrum produced by the emission of light by atoms in excited states.. The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrumA spectrum produced by the absorption of light by ground-state atoms.. Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter, as we describe in Section 1.3 .

### Note the Pattern

When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

## Applications of Emission and Absorption Spectra

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

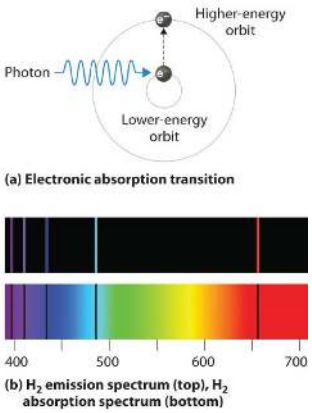



Figure 2.3.6 Absorption and Emission Spectra *(a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.*

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the

composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 2.3.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning "sun." Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium, pick up electrons from the rocks to form helium atoms.

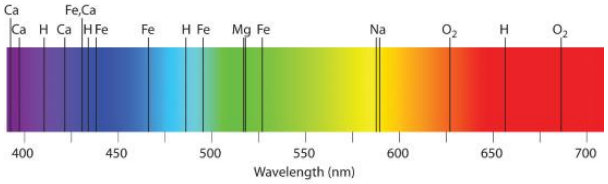



Figure 2.3.7 The Visible Spectrum of **Sunlight***The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.*

The familiar red color of "neon" signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 2.3.5 . Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 2.3.5 ). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

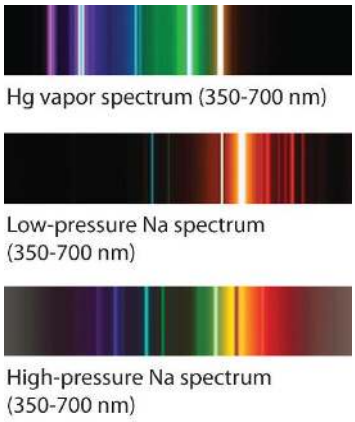



Figure 2.3.8 The emission spectra of sodium and **mercury** *Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.*




Figure 2.3.9 The Chemistry of Fireworks *(a) In the "multibreak" shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.*

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure 2.3.9 , a typical shell used in a fireworks display contains gunpowder to propel the shell into the air and a fuse to initiate a variety of reactions that produce heat and small explosions. Thermal energy excites the atoms to higher energy states; as they decay to lower energy states, the atoms emit light that gives the familiar colors. When oxidant/reductant mixtures listed in Table 2.3.1 are ignited, a flash of white or yellow light is produced along with a loud bang. Achieving the colors shown in part (b) in Figure 2.15 requires adding a small amount of a substance that has an emission spectrum in the desired portion of the visible spectrum. For example, sodium is used for yellow because of its 589 nm emission lines. The intense yellow color of sodium would mask most other colors, so potassium and ammonium salts, rather than sodium salts, are usually used as oxidants to produce other colors, which explains the preponderance of such salts in Table 2.3.1. Strontium salts, which are also used in highway flares, emit red light, whereas barium gives a green color. Blue is one of the most difficult colors to achieve. Copper(II) salts emit a pale blue light, but copper is dangerous to use because it forms highly unstable explosive compounds with anions such as chlorate. As you might guess, preparing fireworks with the desired properties is a complex, challenging, and potentially hazardous process. If you have the time here is a NOVA program about how fireworks are made




Oh heck, take a look:)

**Table 2.3.1 Common Chemicals Used in the Manufacture of Fireworks***

| Oxidizers | Fuels (reductants) | Special effects |
|---|---|---|
| ammonium perchlorate | aluminum | *blue flame*: copper carbonate, copper sulfate, or copper oxide |
| barium chlorate | antimony sulfide | *red flame*: strontium nitrate or strontium carbonate |
| barium nitrate | charcoal | *white flame*: magnesium or aluminum |
| potassium chlorate | magnesium | *yellow flame*: sodium oxalate or cryolite ($Na_3AlF_6$) |
| potassium nitrate | sulfur | *green flame*: barium nitrate or barium chlorate |
| potassium perchlorate | titanium | *white smoke*: potassium nitrate plus sulfur |
| strontium nitrate | | *colored smoke*: potassium chlorate and sulfur, plus organic dye |
| | | *whistling noise*: potassium benzoate or sodium salicylate |
| | | *white sparks*: aluminum, magnesium, or titanium |
| | | *gold sparks*: iron fillings or charcoal |
| *Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect. | | |

## Lasers

Most light emitted by atoms is *polychromatic*—containing more than one wavelength. In contrast, *lasers* (from *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation) emit *monochromatic* light—a single wavelength only. Lasers have many applications in fiber-optic telecommunications, the reading and recording of compact discs (CDs) and digital video discs (DVDs), metal cutting, semiconductor fabrication, supermarket checkout scanners and laser pointers. Laser beams are generated by the same general phenomenon that gives rise to emission spectra, with one difference: only a single excited state is produced, which in principle results in only a single frequency of emitted light. In practice, however, inexpensive commercial lasers actually emit light with a very narrow range of wavelengths.

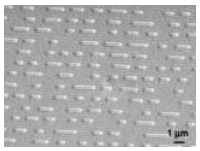


Figure 2.3.10 **How a CD player uses a laser to read a CD** *Inside a CD is a flat, light-reflecting layer called "land." On the land are many "pits" recorded in a spiral-shaped track. (From the laser's point of view, pits are actually the "bumps" shown here because the master disc with pits is duplicated negatively, turning the pits into bumps.) The pits spread (scatter) the reflected light. The amount of light reflected directly into the detactor by pits is low compared with that reflected by land.*

The operation of a ruby laser, the first type of laser to be demonstrated, is shown schematically in Figure 2.16 Ruby is an impure form of aluminum oxide ($Al_2O_3$) in which $Cr^{3+}$ replaces some of the $Al^{3+}$ ions. The red color of the gem is caused by the absorption of light in the blue region of the visible spectrum by $Cr^{3+}$ ions, which leaves only the longer wavelengths to be reflected back to the eye. One end of a ruby bar is coated with a fully reflecting mirror, and the mirror on the other end is only partially reflecting. When flashes of white light from a flash lamp excite the $Cr^{3+}$ ions, they initially decay to a relatively long-lived excited state and can subsequently decay to the ground state by emitting a photon of red light. Some of these photons are reflected back and forth by the mirrored surfaces. As shown in part (b) in Figure 2.3.11 , each time a photon interacts with an excited $Cr^{3+}$ ion, it can stimulate that ion to emit another photon that has the same wavelength and is synchronized (*in phase*) with the first wave. This process produces a *cascade* of photons traveling back and forth, until the intense beam emerges through the partially reflecting

mirror. Ruby is only one substance that is used to produce a laser; the choice of material determines the wavelength of light emitted, from infrared to ultraviolet, and the light output can be either continuous or pulsed.

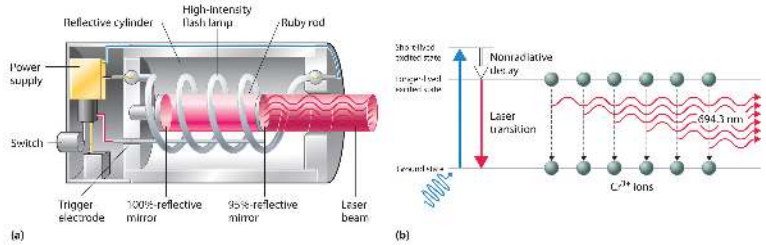



Figure 2.3.11 A Ruby Laser *(a) This cutaway view of a ruby laser shows the ruby rod, the flash lamp used to excite the $Cr^{3+}$ ions in the ruby, and the totally and partially reflective mirrors. (b) This schematic drawing illustrates how light from the flash lamp excites the $Cr^{3+}$ ions to a short-lived excited state, which is followed by decay to a longer-lived excited state that is responsible for the stimulated in-phase emission of light by the laser.*

When used in a DVD player or a CD player, light emitted by a laser passes through a transparent layer of plastic on the CD and is reflected by an underlying aluminum layer, which contains pits or flat regions that were created when the CD was recorded. Differences in the frequencies of the transmitted and reflected light are detected by light-sensitive equipment that converts these differences into binary code, a series of 1s and 0s, which is translated electronically into recognizable sounds and images.

## Key Equation

**Rydberg equation**

**Equation 2.3.1:** $\frac{1}{\lambda} = \Re \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

## Summary

Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element.

## Key Takeaway

- There is an intimate connection between the atomic structure of an atom and its spectral characteristics.

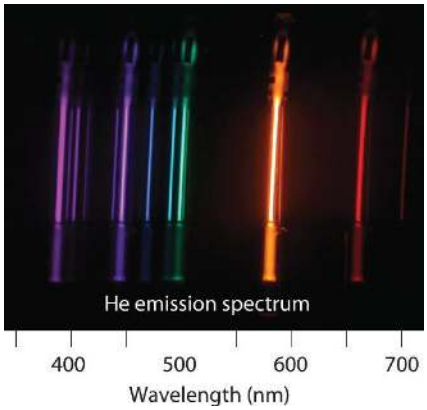
## Conceptual Problems

1. Is the spectrum of the light emitted by isolated atoms of an element discrete or continuous? How do these spectra differ from those obtained by heating a bulk sample of a solid element? Explain your answers.
2. Explain why each element has a characteristic emission and absorption spectra. If spectral emissions had been found to be continuous rather than discrete, what would have been the implications for Bohr's model of the atom?
3. Explain the differences between a ground state and an excited state. Describe what happens in the spectrum of a species when an electron moves from a ground state to an excited state. What happens in the spectrum when the electron falls from an excited state to a ground state?

4. What phenomenon causes a neon sign to have a characteristic color? If the emission spectrum of an element is constant, why do some neon signs have more than one color?
5. How is light from a laser different from the light emitted by a light source such as a light bulb? Describe how a laser produces light.

## Numerical Problems

1. Using a Bohr model and the transition from $n = 2$ to $n = 3$ in an atom with a single electron, describe the mathematical relationship between an emission spectrum and an absorption spectrum. What is the energy of this transition? What does the sign of the energy value represent in this case? What range of light is associated with this transition?
2. If a hydrogen atom is excited from an $n = 1$ state to an $n = 3$ state, how much energy does this correspond to? Is this an absorption or an emission? What is the wavelength of the photon involved in this process? To what region of the electromagnetic spectrum does this correspond?
3. The hydrogen atom emits a photon with a 486 nm wavelength, corresponding to an electron decaying from the $n = 4$ level to which level? What is the color of the emission?
4. An electron in a hydrogen atom can decay from the $n = 3$ level to $n = 2$ level. What is the color of the emitted light? What is the energy of this transition?
5. Calculate the wavelength and energy of the photon that gives rise to the third line in order of increasing energy in the Lyman series in the emission spectrum of hydrogen. In what region of the spectrum does this wavelength occur? Describe qualitatively what the absorption spectrum looks like.
6. The wavelength of one of the lines in the Lyman series of hydrogen is 121 nm. In what region of the spectrum does this occur? To which electronic transition does this correspond?
7. The emission spectrum of helium is shown. Estimate what change in energy ($\Delta E$) gives rise to each line?




8. Removing an electron from solid potassium requires 222 kJ/mol. Would you expect to observe a photoelectric effect for potassium using a photon of blue light ($\lambda = 485$ nm)? What is the longest wavelength of energy capable of ejecting an electron from potassium? What is the corresponding color of light of this wavelength?
9. The binding energy of an electron is the energy needed to remove an electron from its lowest energy state. According to Bohr's postulates, calculate the binding energy of an electron in a hydrogen atom. There are $6.02 \times 10^{23}$ atoms in 1g of hydrogen atoms What wavelength in nanometers is required to remove such an electron from one hydrogen atom?
10. As a radio astronomer, you have observed spectral lines for hydrogen corresponding to a state with $n = 320$, and you would like to produce these lines in the laboratory. Is this feasible? Why or why not?

## Answers

1. 656 nm; red light
2.

3. $n = 2$, blue-green light
4. 
5. 97.2 nm, $2.04 \times 10^{-18}$ J/photon, ultraviolet light, absorption spectrum is a single dark line at a wavelength of 97.2 nm
6. 
7. Violet: 390 nm, 307 kJ/mol photons; Blue-purple: 440 nm, 272 kJ/mol photons; Blue-green: 500 nm, 239 kJ/mol photons; Orange: 580 nm, 206 kJ/mol photons; Red: 650 nm, 184 kJ/mol photons
8. 
9. 1313 kJ/mol, $\lambda \leq 91.1$ nm
10. 

## Contributors

- Anonymous

Modified by Joshua Halpern

Structure of the Atom Video from SteveVD1 on YouTube

NOVA Fireworks Video from Burning Salvo on YouTube

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# 6.4: Wave - Particle Duality

**Learning Objectives**

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

## The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle dualityA principle that matter and energy have properties typical of both waves and particles.. Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv}$$

where *h* is Planck's constant, *m* is the mass of the particle, and *v* is the velocity of the particle. This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 4, Planck's constant ($6.63 \times 10^{-34}$ J·s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

### Example 2.4.1

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

**Given:** mass and speed of object

**Asked for:** wavelength

**Strategy:**

**A** Convert the speed of the baseball to the appropriate SI units: meters per second.

**B** Substitute values into Equation 2.4.3 and solve for the wavelength.

**Solution:**

The wavelength of a particle is given by λ = *h*/*mv*. We know that *m* = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

**B** Recall that the joule is a derived unit, whose units are (kg·m$^2$)/s$^2$. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s}^{-1}\right)} = 9.95 \times 10^{-35}\ m$$

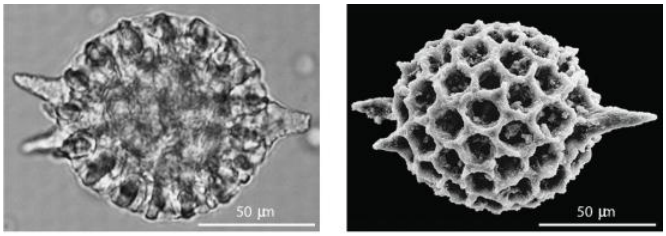
(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately $10^{-14}$ m, the wavelength of the baseball is almost unimaginably small.

Exercise

Calculate the wavelength of a neutron that is moving at 3.00 × 10$^3$ m/s.

**Answer:** 1.32 Å, or 132 pm

As you calculated in Example 4, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, such as electrons, exhibit the properties of both particles and waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 2.4.1 ).




(a) Radiolarian under light microscope (b) Radiolarian under electron microscope

Figure 2.4.1 A Comparison of Images Obtained Using a Light Microscope and an Electron **Microscope** *Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)*

## An Important Wave Property - Phase

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the **relative** displacement of two waves called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 2.18a, on the right shows an arbitrary phase difference between two wave. Figure 2.18b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 2.18 c shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities.

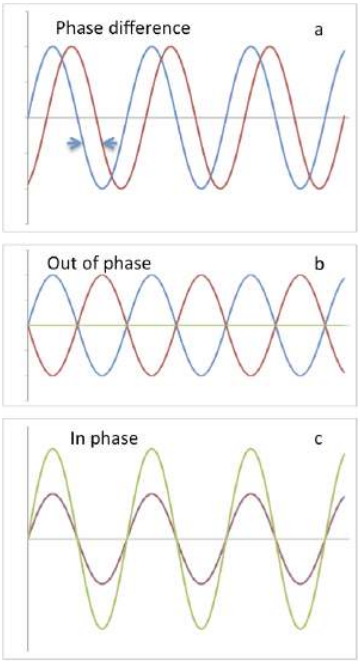
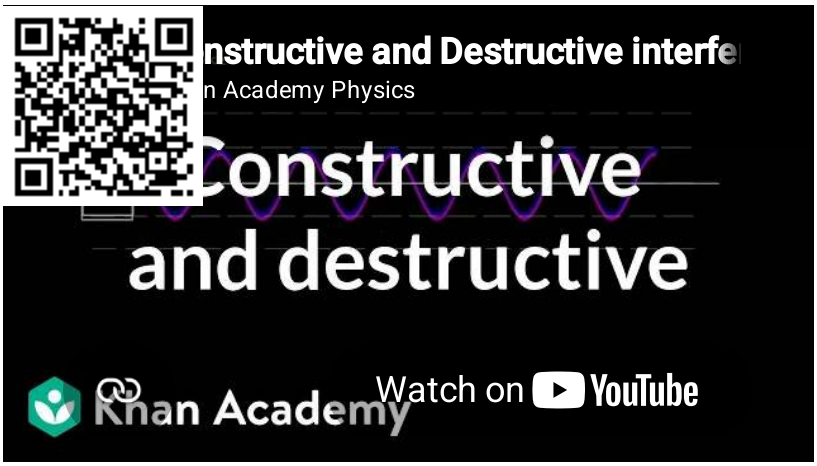



Figure 2.4.2 **Phase** *Two waves travelling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase diffence is 180 they completely cancel each other out.*

A more detailed explanation can be seen in the video below if you are attached to the INTERNET.




## Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a standing waveA wave that does not travel in space., a wave that does not travel in space. An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 2.4.3 ). If the length of the string is $L$, then the lowest-energy vibration (the fundamentalThe lowest-energy standing wave.) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L$$

Higher-energy vibrations (overtonesThe vibration of a standing wave that is higher in energy than the fundamental vibration.) are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n}$$

where *n* has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. By analogy we can think of the resonant frequencies as being quantized. Notice in Figure 2.4.3 that all overtones have one or more nodesThe point where the amplitude of a wave is zero., points where the string does not move. The amplitude of the wave at a node is zero.

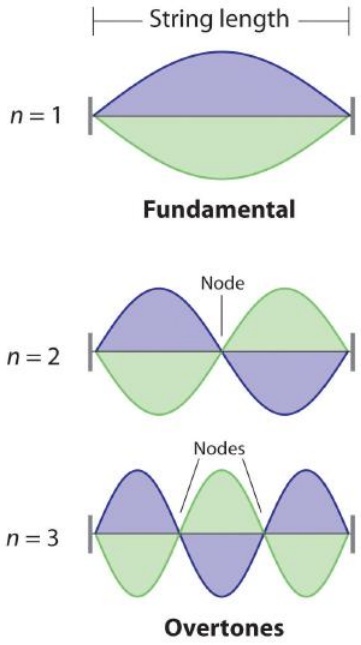



Figure 2.4.3 Standing Waves on a Vibrating String *The vibration with n = 1 is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain n − 1 nodes.*

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda$$

where *r* is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 2.4.4 ). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference.* The non resonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to *n* = 1 in Equation 2.18, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Still, as all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far can mislead.

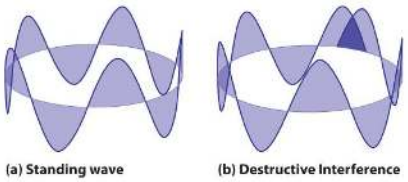



Figure 2.4.4 Standing Circular Wave and Destructive Interference *(a) In a standing circular wave with n = 5, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.*

As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases.

Unfortunately, his (and Bohr's) explanation also contains one major feature that we know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

### Videos

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite

### Examples

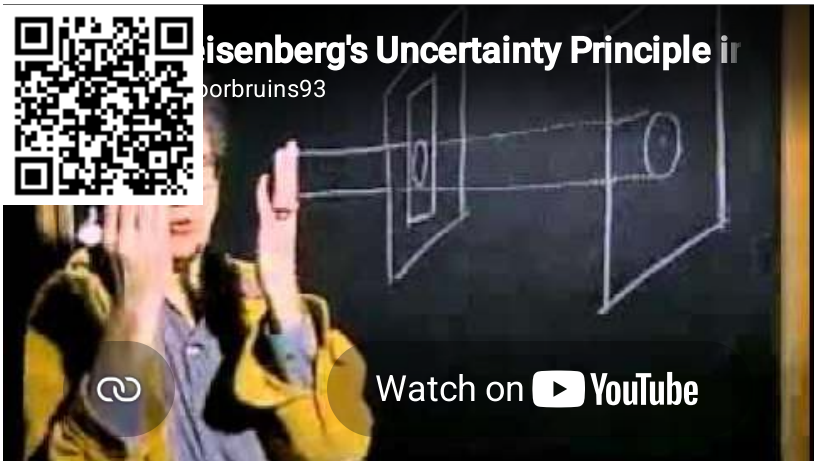
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

## The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit as shown in the video below. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new




DeBroglie's idea of wave particle duality means that particles such as electronx which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that “at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation.” Mathematically, the Heisenberg uncertainty principleA principle stating that the uncertainty in the position of a particle *Δx* multiplied by the uncertainty in its momentum *Δ(mv)* is greater than or equal to Planck’s constant *h* divided by 4π: states that the uncertainty in the position of a particle (Δ*x*) multiplied by the uncertainty in its momentum [Δ(*mv*)] is greater than or equal to Planck’s constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

Because Planck’s constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie’s equation to have measurable wavelengths.

If the precise position *x* of a particle is known absolutely (Δ*x* = 0), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty$$

Because the mass of the electron at rest (*m*) is both constant and accurately known, the uncertainty in Δ(*mv*) must be due to the Δ*v* term, which would have to be infinitely large for Δ(*mv*) to equal infinity. That is, according to Equation 2.20, the more accurately we know the exact position of the electron (as Δ*x* → 0), the less accurately we know the speed and the kinetic energy of the electron (1/2 $mv^2$) because Δ(*mv*) → ∞. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as Δ(*mv*) → 0], then Δ*x* → ∞ and we have no idea where the electron is.

The Heisenberg Uncertainty Principle is an application of deBroglie's wave particle duality to wave diffraction.

Bohr’s model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify simultaneously both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr’s model.

### Example 2.4.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 4 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

**Given:** mass and speed of object

**Asked for:** minimum uncertainty in its position

**Strategy:**

**A** Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 2.4.7) to solve for the minimum uncertainty in the position of an object ($\Delta x$).

**B** Find $\Delta v$ by converting the velocity of the baseball to the appropriate SI units: meters per second.

**C** Substitute the appropriate values into the expression for the inequality and solve for $\Delta x$.

**Solution:**

**A** The Heisenberg uncertainty principle tells us that $(\Delta x)[\Delta(mv)] = h/4\pi$. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

**B** We know that $h = 6.626 \times 10^{-34}$ J·s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

$$\Delta v = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s$$

**C Therefore,**

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg·m$^2$/s$^2$) gives

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34}\ m$$

This is equal to $3.12 \times 10^{-32}$ inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

**Answer:** $6 \times 10^{-10}$ m, or 0.6 nm (about the diameter of a benzene molecule)

## Key Equations

**De Broglie's relationship between mass, speed, and wavelength**

Equation 2.4.3: $\lambda = \dfrac{h}{mv}$

**Heisenberg's uncertainty principle**

Equation 2.4.7: $(\Delta x)\,(\Delta\,[mv]) \geqslant \dfrac{h}{4\pi}$

## Summary

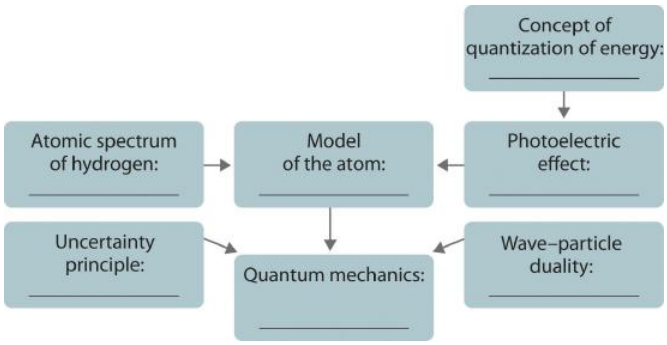
The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle. The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

## Key Takeaway

- An electron possesses both particle and wave properties.

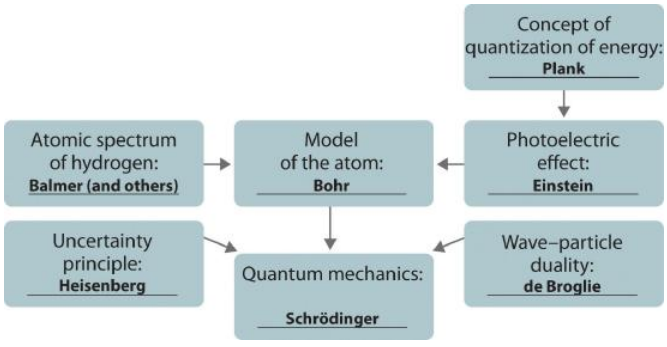
## Conceptual Problems

1. Explain what is meant by each term and illustrate with a sketch:
    1. standing wave
    2. fundamental
    3. overtone
    4. node
2. How does Einstein's theory of relativity illustrate the wave–particle duality of light? What properties of light can be explained by a wave model? What properties can be explained by a particle model?
3. In the modern theory of the electronic structure of the atom, which of de Broglie's ideas have been retained? Which proved to be incorrect?
4. According to Bohr, what is the relationship between an atomic orbit and the energy of an electron in that orbit? Is Bohr's model of the atom consistent with Heisenberg's uncertainty principle? Explain your answer.
5. The development of ideas frequently builds on the work of predecessors. Complete the following chart by filling in the names of those responsible for each theory shown.




## Answer

1.
2.
3.
4.
5.




## Numerical Problems

1. How much heat is generated by shining a carbon dioxide laser with a wavelength of 1.065 μm on a 68.95 kg sample of water if 1.000 mol of photons is absorbed and converted to heat? Is this enough heat to raise the temperature of the water 4°C?

2. Show the mathematical relationship between energy and mass and between wavelength and mass. What is the effect of doubling the
    1. mass of an object on its energy?
    2. mass of an object on its wavelength?
    3. frequency on its mass?
3. What is the de Broglie wavelength of a 39 g bullet traveling at 1020 m/s ± 10 m/s? What is the minimum uncertainty in the bullet's position?
4. What is the de Broglie wavelength of a 6800 tn aircraft carrier traveling at 18 ± 0.1 knots (1 knot = 1.15 mi/h)? What is the minimum uncertainty in its position?
5. Calculate the mass of a particle if it is traveling at $2.2 \times 10^6$ m/s and has a frequency of $6.67 \times 10^7$ Hz. If the uncertainty in the velocity is known to be 0.1%, what is the minimum uncertainty in the position of the particle?
6. Determine the wavelength of a 2800 lb automobile traveling at 80 mi/h ± 3%. How does this compare with the diameter of the nucleus of an atom? You are standing 3 in. from the edge of the highway. What is the minimum uncertainty in the position of the automobile in inches?

## Answers

1. $E$ = 112.3 kJ, $\Delta T$ = 0.3893°C, over ten times more light is needed for a 4.0°C increase in temperature
2. 
3. $1.7 \times 10^{-35}$ m, uncertainty in position is $\geq 1.4 \times 10^{-34}$ m
4. 
5. $9.1 \times 10^{-39}$ kg, uncertainty in position ≥ 2.6 m
6. 

## Contributors

- Anonymous

Modified by Joshua Halpern

Constructive and Destructive Interference Video from Khan Academy on YouTube

Heiserberg Uncertainty Video by Walter Lewin from YouTube

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# 6.5: Atomic Orbitals and Their Energies

**Learning Objectives**

- To apply the results of quantum mechanics to chemistry

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. In doing so, Schrödinger's theory today is described as quantum mechanicsA theory developed by Erwin Schrödinger that describes the energies and spatial distributions of electrons in atoms and molecules.. It successfully describes the energies and spatial distributions of electrons in atoms and molecules.

### Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger's equations. The Schrödinger equation is similar in form to equations for the propagation of waves, which is why originally quantum mechanics was called wave mechanics, but there are significant differences between quantum wave functions and those that describe real waves. Therefore, at this point it would be best to lean only lightly on the standing wave analogy.

## Wave Functions

A wavefunction (Ψ)A mathematical function that relates the location of an electron at a given point in space to the amplitude of its wave, which corresponds to its energy., Ψ is the uppercase Greek letter psi, is a mathematical expression that can be used to calculate any property of an atom. In general, wavefunctions depend on both time and position. For atoms, solutions to the Schrödinger equation correspond to arrangements of the electrons, which, if left alone, remain unchanged and are thus only functions of position. To indicate time independence we use lower case ψ

Wavefunctions for each atom have some properties that are exact, for example each wavefunction describes an electron in quantum state with a specific energy. Each of these exact properties is associated with an integer. The energy of an electron in an atom is associated with the integer $n$, which turns out to be the same $n$ that Bohr found in his model. These integers are called quantum numbers and different wavefunctions have different sets of quantum numbers. The important point about quantum numbers is that they are countable integers, not continuous variables like the number of points on a line. In the case of atoms, each electron has four quatum numbers which determine its wavefunction.

For other properties, there is a mathematical procedure by which the wavefunctions can be used to calculate average values and probabilities for anything, for example the probability of finding the electron at any point in space. Driven by the Heisenberg Uncertainy Principle, the calculation of probabilities is the best we can do for properties not associated directly with quantum numbers.

The properties of wave functions derived from quantum mechanics are summarized here. Although there are no equations there are a number of advanced concepts. Even if your math is not strong, try to understand the key concepts.:

- **A time independent wavefunction uses three variables to describe the position of an electron.** Three coordinates specify the position in space (as with the Cartesian coordinates $x$, $y$, and $z$, or spherical coordinates $r$, $\theta$, $\varphi$). Figure 2.21 shows both Cartesian and spherical coordinates. For the motion of an electron about the massive nucleus, spherical coordinates can be more natural than Cartesian.

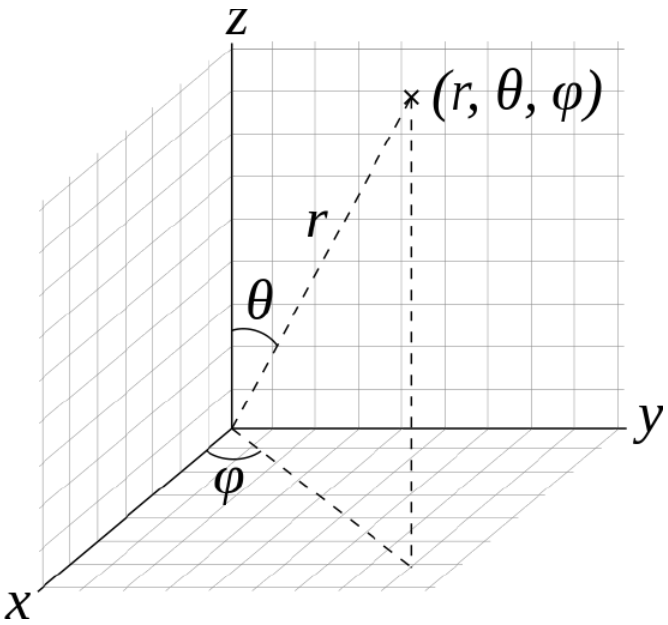
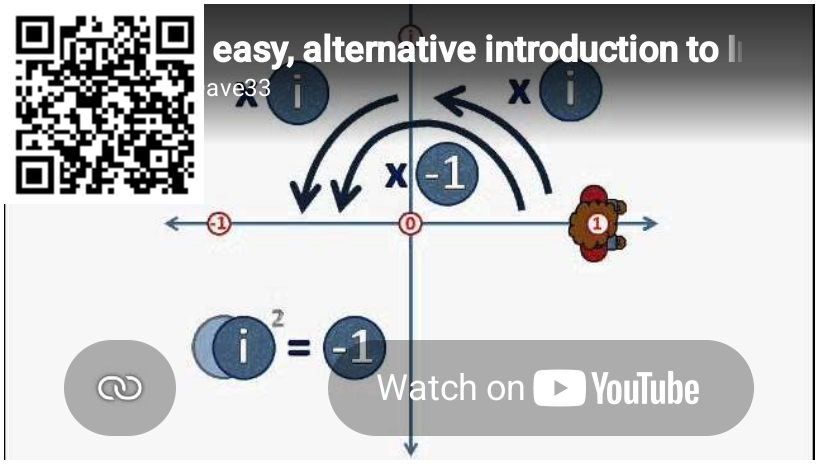


Figure 2.5.1 Cartesian (x, y, z) and spherical coordinates (r, θ, φ)

- **Wave functions have both real and imaginary parts. They are complex functions**, which is a mathematical term indicating that they contain $\sqrt{-1}$., represented as *i*. Imaginary and complex numbers have no physical significance.

### Imaginary Numbers

If you need an introduction to imaginary number, here is one. To see it you will have to be attached to the INTERNET




- **The probability of finding an electron at a point is given by the product of the wave function ψ and its complex conjugate ψ* in which all terms that contain *i* are replaced by −*i*.** This product is called the modulus square and for wave functions it always must be a real positive number or zero. Negative, impaginary or complex probabilities of finding an electron at a point would be meaningless. This interpretation was discovered by Max Born, for which he won the Nobel prize. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron.

The probability of finding an electron at any point in space depends on several factors, including the quantum numbers specifying the wavefunction and the three coordinates specifying the position in space we are interested in. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, shown for the ground state of the hydrogen atom in Figure 2.5.2

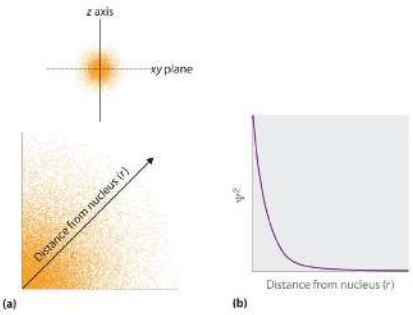



Figure 2.5.2 Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space *(a) The density of the dots shows electron probability. (b) In this plot of $\Psi^2$ versus r for the ground state of the hydrogen atom, the electron probability density is greatest at r = 0 (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but not zero.*

- **The total probability of finding the electron anywhere must be 100%**. It has to be somewhere. On the other hand, since there is a lot more space far away from a nucleus than near it, the probability of finding the electron at any one point as one moves away from the nucleus must eventually go to zero.
- **The relative phases of wave function for electrons in different atoms** determines bonding. This will be important in our discussion of chemical bonding in Chapter 5. As discussed in the previous section, wavefunctions like waves, can positively reinforce each other or destructively interfere. When they reinforce they are said to be in phase, and when they interfere they are said to be out of phase. The phases are indicated as positive, +, or negative, -. Do not confuse the sign of the phase with a positive or negative electrical charge.
- **Each wavefunction has a unique sets of** quantum numbersA unique set of numbers that specifies a wave function (a solution to the Schrödinger equation), which provides important information about the energy and spatial distribution of an electron.**.** The spacial patterns of the three-dimensional wave functions are complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a water world, which turn out to be solutions of the Schrödinger equation for a spherically symmetric atom.
- **Each wave function is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization emerges from the wave equation.

## Quantum Numbers

Schrödinger's approach requires three quantum numbers ($n$, $l$, and $m_l$) to specify a wave function for each electron. The quantum numbers provide information about the spatial distribution of an electron. Although $n$ can be any positive integer (NOT zero), only certain values of $l$ and $m_l$ are allowed for a given value of $n$. This is a consequence of the mathematical details of the Schrödinger equation

## The Principal Quantum Number

The principal quantum number ($n$)One of three quantum numbers that tells the average relative distance of an electron from the nucleus. indicates the energy of the electron and the average distance of an electron from the nucleus:

**Equation 2.5.1** $n = 1, 2, 3, 4,\ldots$

As $n$ increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of $n$ are easier to remove from an atom. All wave functions that have the same value of $n$ are said to constitute a principal shellAll the wave functions that have the same value of because those electrons have similar average distances from the nucleus. because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number $n$ corresponds to the $n$ used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

## The Azimuthal Quantum Number

The second quantum number is often called the azimuthal quantum number ($l$)One of three quantum numbers that discribes the shape of the region of space occupied by an electron.. The value of $l$ describes the *shape* of the region of space occupied by the electron. The allowed values of $l$ depend on the value of $n$ and can range from 0 to $n − 1$:

**Equation 2.5.2** $l = 0, 1, 2,\ldots, n − 1$

For example, if $n = 1$, $l$ can be only 0; if $n = 2$, $l$ can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both $n$ and $l$ form a subshellA group of wave functions that have the same values of <math xml:id="av_1.0-ch02_m046" display="inline"><semantics><mi>n</mi></semantics></math> and <math xml:id="av_1.0-ch02_m047" display="inline"><semantics><mrow><mi>l</mi><mo>.</mo></mrow></semantics></math>. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

## The Magnetic Quantum Number

The third quantum number is the magnetic quantum number ($m_l$)One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.. The value of $m_l$ describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of $m_l$ depend on the value of $l$: $m_l$ can range from $−l$ to $l$ in integral steps:

**Equation 2.5.3** $m_l = −l, −l + 1,\ldots, 0,\ldots, l − 1, l$

For example, if $l = 0$, $m_l$ can be only 0; if $l = 1$, $m_l$ can be −1, 0, or +1; and if $l = 2$, $m_l$ can be −2, −1, 0, +1, or +2.

Each wave function with an allowed combination of $n$, $l$, and $m_l$ values describes an atomic orbital A wave function with an allowed combination of n, l and $m_l$ quantum numbers., a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

### Example 2.5.1

How many subshells and orbitals are contained within the principal shell with $n = 4$?

**Given:** value of $n$

**Asked for:** number of subshells and orbitals in the principal shell

**Strategy:**

**A** Given $n = 4$, calculate the allowed values of $l$. From these allowed values, count the number of subshells.

**B** For each allowed value of $l$, calculate the allowed values of $m_l$. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

**Solution:**

**A** We know that $l$ can have all integral values from 0 to $n − 1$. If $n = 4$, then $l$ can equal 0, 1, 2, or 3. Because the shell has four values of $l$, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of $m_l$.

**B** For $l = 0$, $m_l$ can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, $m_l$ can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, $m_l$ can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of $l$ is $l = 3$, for which $m_l$ can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2$:

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

Exercise

How many subshells and orbitals are in the principal shell with $n = 3$?

**Answer:** three subshells; nine orbitals

Rather than specifying all the values of $n$ and $l$ every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of $l$ for a particular subshell or orbital:

| $l$ = | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| **Designation** | *s* | *p* | *d* | *f* |

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics of lines involving them: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental. A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 2.5.1 ):

- Each principal shell has $n$ subshells. For $n = 1$, only a single subshell is possible (1*s*); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of $l$ for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

### Note the Pattern

Each principal shell has $n$ subshells, and each subshell has $2l + 1$ orbitals.

**Table 2.5.1 Allowed values of *n*, *l*, and $m_l$ through *n* = 4**

| $n$ | $l$ | Subshell Designation | $m_l$ | Number of Orbitals in Subshell | Number of Orbitals in Shell |
|---|---|---|---|---|---|
| 1 | 0 | 1*s* | 0 | 1 | 1 |
| 2 | 0 | 2*s* | 0 | 1 | 4 |
| | 1 | 2*p* | −1, 0, 1 | 3 | |
| 3 | 0 | 3*s* | 0 | 1 | 9 |
| | 1 | 3*p* | −1, 0, 1 | 3 | |
| | 2 | 3*d* | −2, −1, 0, 1, 2 | 5 | |
| 4 | 0 | 4*s* | 0 | 1 | 16 |
| | 1 | 4*p* | −1, 0, 1 | 3 | |
| | 2 | 4*d* | −2, −1, 0, 1, 2 | 5 | |
| | 3 | 4*f* | −3, −2, −1, 0, 1, 2, 3 | 7 | |

### Videos

- Quantum numbers - ChemDo

### Examples

- Quantum Numbers and Electron Configurations - Purdue - tutorial
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

## Orbital Shapes

An orbital is the quantum mechanical generalization of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

One way of representing electron probability distributions was illustrated in Figure 2.5.1 for the 1*s* orbital of hydrogen. The probability of finding an electron in a region of space with volume V (such as a cubic picometer) is the product of the volume with $\psi\psi^*$(we can write this as $|\psi|^2$). From our consideration of the properties of the wavefunction, we know that adding up the probability from every such small volume over all space will sum to unity, or a 100% probability that the electron is somewhere. A plot of $|\psi|^2$ versus distance from the nucleus ($r$) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of $r$, the electron probability density is tiny but *not* eactly zero.

In contrast to the probability density, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance $r$ from the nucleus) by adding together the probabilities of an electron being at all points on a series of $x$ spherical shells of radius $r_1$, $r_2$, $r_3$,…, $r_{x-1}$, $r_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 2.5.2 ), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 2.5.3 ), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 2.5.3

By contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases rapidly with increasing $r$ (part (c) in Figure 2.5.3 ). Because the surface area of the spherical shells increases at first more rapidly with increasing $r$ than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 2.5.3 ). As important, when $r$ is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes because the surface area of the shell is zero (part (d) in Figure 2.5.2 ).

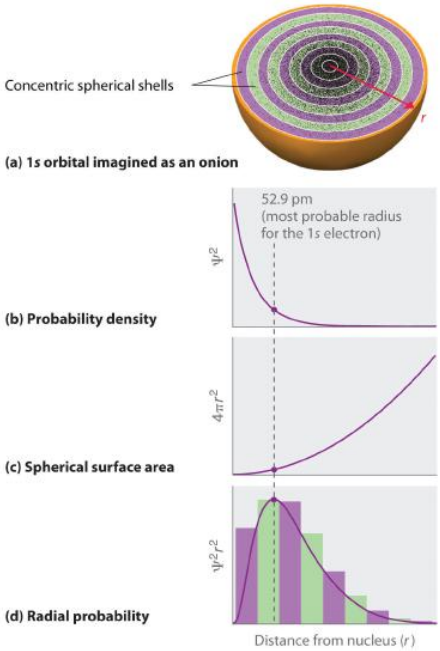



Figure 2.5.3 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom *(a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density $\Psi^2$ versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.*

For the hydrogen atom, the peak in the radial probability plot occurs at $r$ = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the $n$ = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg Uncertainty Principle.

Figure 2.5,4 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 2.5.4 ). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

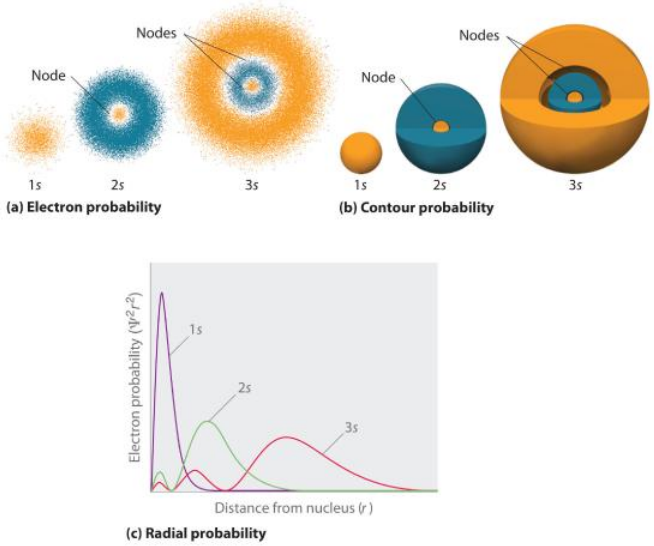



Figure 2.5.4 Probability Densities for the 1*s*, 2*s*, and 3*s* Orbitals of the Hydrogen Atom *(a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r.*

## *s* Orbitals

Three things happen to *s* orbitals as *n* increases (Figure 2.5.4 ):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron densityElectron distributions that are represented as standing waves., as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 2.5.4 Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding. This makes sense because bonding is an interaction of electrons from two atoms which will be most sensitive to forces at the edges of the orbitals.

## *p* Orbitals

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of $m_l$ (−1, 0, and +1), there are three 2*p* orbitals.

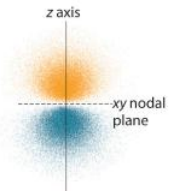



Figure 2.5.4 , the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 2.5.5 . Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 2.5.6 , the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

In the next section when we consider the electron configuration of multielectron atoms, the geometric shapes provide an important clue about which orbitals will be occupied by different electrons. Because electrons in different *p* orbitals are geometrically distant from each other, there is less repulsion between them than would be found if two electrons were in the same *p* orbital. Thus, when the *p* orbitals are filled, it will be energetically favorable to place one electron into each *p* orbital, rather than two into one orbital.

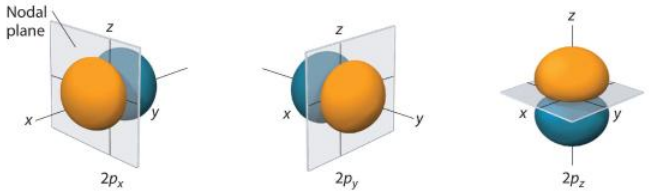



Figure 2.5.6 The Three Equivalent 2*p* Orbitals of the Hydrogen **Atom***The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2p orbital. The phase of the wave function is positive (orange) in the region of space where x, y, or z is positive and negative (blue) where x, y, or z is negative.*

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 2.5.6

## *d* Orbitals

Subshells with $l = 2$ have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to $n = 3$. The five *d* orbitals have $m_l$ values of −2, −1, 0, +1, and +2.

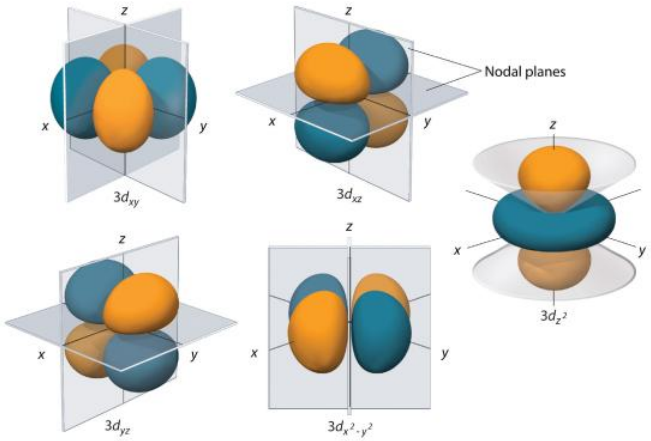



Figure 2.5.7 The Five Equivalent 3*d* Orbitals of the Hydrogen Atom *The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$ , has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.*

The hydrogen 3*d* orbitals, shown in Figure 2.5.7 , have more complex shapes than the 2*p* orbitals. All five 3*d* orbitals contain two nodal surfaces, as compared to one for each *p* orbital and zero for each *s* orbital. In three of the *d* orbitals, the lobes of electron density are oriented between the *x* and *y*, *x* and *z*, and *y* and *z* planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth *d* orbital has lobes lying along the *x* and *y* axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3*d* orbital, called the $3d_{z^2}$

orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the *xy* plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to *p* orbitals, the phase of the wave function for *d* orbitals is the same for opposite pairs of lobes. As shown in Figure 2.5.7 , the phase of the wave function is positive for the two lobes of the $3d_{z^2}$ orbital that lie along the *z* axis, whereas the phase of the wave function is negative for the doughnut of electron density in the *xy* plane. Like the *s* and *p* orbitals, as *n* increases, the size of the *d* orbitals increases, but the overall shapes remain similar to those depicted in Figure 2.5.7 .

## *f* Orbitals

Principal shells with $n = 4$ can have subshells with $l = 3$ and $m_l$ values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex. Because *f* orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of *l* are not discussed at all. Equivalent illustrations of the shapes of the f orbitals are available

## Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energiesA particular energy associated with a given set of quantum numbers. by considering atoms or ions with only a single electron (such as H or $He^+$). This is the simplest case.

The relative energies of the atomic orbitals with $n \le 4$ for a hydrogen atom are plotted in Figure 2.5.8 note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.The different values of *l* and $m_l$ for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of *n* (e.g., the three 2*p* orbitals) are degenerateHaving the same energy., meaning that they have the same energy. Figure 2.5.8 shows that the energy levels become closer and closer together as the value of *n* increases, as expected because of the $1/n^2$ dependence of orbital energies.

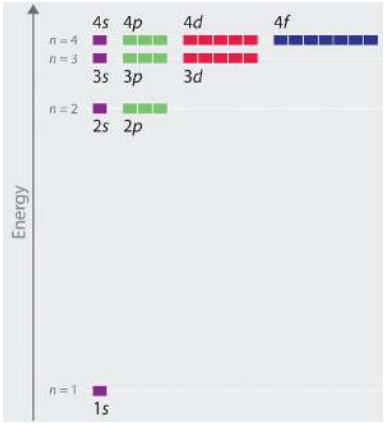



Figure 2.5.8 Orbital Energy Level Diagram for the Hydrogen Atom *Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.*

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation (Equation 2.3.3), which can be extended to other single-electron species by incorporating the nuclear charge *Z* (the number of protons in the nucleus):

**Equation 2.5.4** $E = -\frac{Z^2}{n^2}\mathcal{R}hc$

In general, both energy and radius decrease as the nuclear charge increases. As a result of the $Z^2$ dependence of energy in Equation 2.24, electrons in the 1s orbital of carbon, which has a nuclear charge of +6, lie roughly 36 times lower in energy than those in the hydrogen 1s orbital, and the 1s orbital of tin, with an atomic number of 50 is roughly 2500 times lower still. The most stable and tightly bound electrons are in orbitals (those with the lowest energy) closest to the nucleus.

For example, in the ground state of the hydrogen atom, the single electron is in the 1*s* orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the $n = 2$ orbitals. In ions with only a single electron, the energy of a given orbital depends on only $n$, and all subshells within a principal shell, such as the $p_x$, $p_y$, and $p_z$ orbitals, are degenerate.

### Videos

- Quantum Mechanics 6a- Hydrogen - via science (don't bother with the first 3 minutes which are advanced math heavy, but the stunning illustrations of orbital shapes afterwards are great)
- Electron Spin and the Pauli Principle - via science.(does an excellent job explaining why electron spin is not a spinning electron)
- Electron Orbitals - Anna Tanczos - more visualizations

### Examples

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

## Effective Nuclear Charges

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance $r$ between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge ($Z_{\text{eff}}$)The nuclear charge an electron actually experiences because of shielding from other electrons closer to the nucleus. that is *less* than the actual nuclear charge $Z$. This effect is called electron shieldingThe effect by which electrons closer to the nucleus neutralize a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between the nucleus and an electron father away.. As the distance between an electron and the nucleus approaches infinity, $Z_{\text{eff}}$ approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{\text{eff}} \approx Z$. At intermediate values of $r$, the effective nuclear charge is somewhere between 1 and $Z$: $1 \le Z_{\text{eff}} \le Z$. Thus the actual $Z_{\text{eff}}$ experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in $Z_{\text{eff}}$ for different elements, as shown in Figure 2.5.9 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{\text{eff}} = Z$, and only for helium are $Z_{\text{eff}}$ and $Z$ comparable in magnitude.

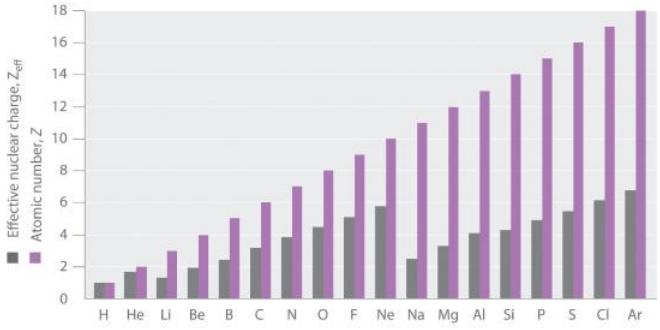



Figure 2.5.9 Relationship between the Effective Nuclear Charge $Z_{eff}$ and the Atomic Number $Z$ for the Outer Electrons of the Elements of the First Three Rows of the Periodic **Table** *Except for hydrogen, $Z_{eff}$ is always less than Z, and $Z_{eff}$ increases from left to right as you go across a row.*

The trend that you see in Figure 2.5.9 for the first three principal shells corresponding to $n$= 1, 2, and 3, continues in the further shells. The atomic number and thus the nuclear charge increase linearly, but the sawtooth pattern for $Z_{eff}$ repeats itself, resetting as the quantum number $n$ changes. Chemical bonding and reactivity involves the sharing or exchange of electrons between atoms. Those electrons which can participate are those held least strongly by the atom, the outermost electrons, which, no matter what the atomic number, and nuclear charge, are bound to their atom by roughly the same energy range because of the shielding effect.

In multielectron atoms this shifts the energies of the different orbitals for a typical multielectron atom as shown in Figure 2.5.10 . Within a given principal shell of a multielectron atom, the orbital energies increase with increasing $l$. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital. These energy differences are caused by the effects of shielding and *penetration*, the extent to which a given orbital lies inside other filled orbitals. As shown in Figure 2.5.11 for example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Hence in an atom with a filled 1*s* orbital, the $Z_{eff}$ experienced by a 2*s* electron is greater than the $Z_{eff}$ experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 2.5.10

## Note the Pattern

Due to electron shielding, $Z_{eff}$ increases more rapidly going across a row of the periodic table than going down a column.

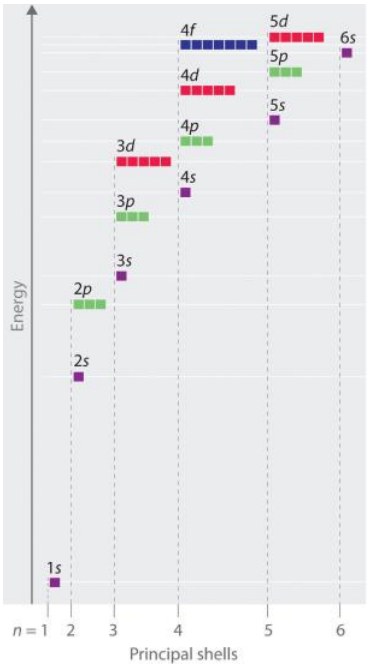



Figure 2.5.10 Orbital Energy Level Diagram for a Typical Multielectron Atom


https://chem.libretexts.org/@go/page/349427

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. (Compare this with Figure 2.5.8 For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

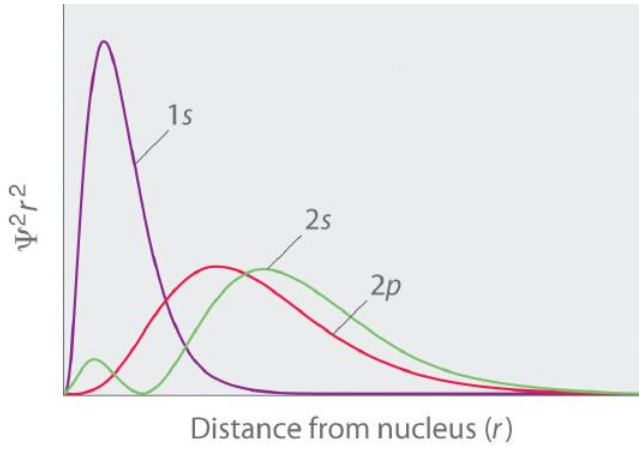



Figure 2.5.11 Orbital Penetration *A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of $Z_{eff}$, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.*

Notice in Figure 2.5.10 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

## Key Equation

**energy of hydrogen-like orbitals**

Equation 2.5.4: $E = -\frac{Z^2}{n^2}\mathcal{R}hc$

## Summary

Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties: (1) the wave function uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron; (2) the magnitude of the wave function is proportional to the intensity of the wave; (3) the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot; (4) describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and (5) each spatial distribution of the electron described by a wave function with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** *n* can be any positive integer; as *n* increases for an atom, the average distance of the electron from the nucleus also increases. All wave functions with the same value of *n* constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** *l* can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. Wave functions that have the same values of both *n* and *l* constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** $m_l$ can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wave function with a given set of values of *n*, *l*, and $m_l$ describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

The four chemically important types of atomic orbital correspond to values of $l$ = 0, 1, 2, and 3. Orbitals with $l$ = 0 are *s* orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $l$ = 0 contain one or more nodes. Orbitals with $l$ = 1 are *p* orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $l$ = 2 are *d* orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $l$ = 3 are *f* orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**. In atoms or ions with only a single electron, all orbitals with the same value of $n$ have the same energy (they are **degenerate**), and the energies of the principal shells increase smoothly as $n$ increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** ($Z_{\text{eff}}$) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of $l$ and the same value of $n$ overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

### Key Takeaway

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

### Conceptual Problems

1. Why does an electron in an orbital with $n$ = 1 in a hydrogen atom have a lower energy than a free electron ($n = \infty$)?
2. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?
3. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?
4. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with $n$ = 2 greater than, less than, or equal to the energy of an orbital with $n$ = 4? Justify your answer.
5. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
    1. 1*s*, 2*p*
    2. 2*p*, 2*s*
    3. 2*s*, 3*s*
    4. 3*d*, 4*s*
6. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
7. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?
8. What quantum number defines each of the following?
    1. the overall shape of an orbital
    2. the orientation of an electron with respect to a magnetic field
    3. the orientation of an orbital in space
    4. the average energy and distance of an electron from the nucleus

9. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

| Element | Number of Electrons | Electrons in orbits with $n$ = | | | |
|---|---|---|---|---|---|
| | | 4 | 3 | 2 | 1 |
| H | 1 | | | | 1 |
| He | 2 | | | | 2 |
| Ne | 10 | | | 8 | 2 |
| Ar | 18 | | 8 | 8 | 2 |
| Li | 3 | | | 1 | 2 |
| Na | 11 | | 1 | 8 | 2 |
| K | 19 | 1 | 8 | 8 | 2 |
| Be | 4 | | | 2 | 2 |

   1. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?
   2. Using Bohr's model, what are the implications for the reactivity of each element?
   3. Give the actual electron configuration of each element in the table.

10. What happens to the energy of a given orbital as the nuclear charge $Z$ of a species increases? In a multielectron atom and for a given nuclear charge, the $Z_{eff}$ experienced by an electron depends on its value of $l$. Why?

11. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.

12. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?

13. Describe the relationship between electron shielding and $Z_{eff}$ on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.

14. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?

   1. 2*s*, 3*s*
   2. 3*p*, 4*d*
   3. 2*p*, 1*s*
   4. 3*d*, 4*s*

## Numerical Problems

1. How many subshells are possible for $n$ = 3? What are they?
2. How many subshells are possible for $n$ = 5? What are they?
3. What value of $l$ corresponds to a *d* subshell? How many orbitals are in this subshell?
4. What value of $l$ corresponds to an *f* subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.

   1. 2*s*
   2. 3*p*
   3. 4*d*

4. 6*f*

6. State the number of orbitals and electrons that can occupy each subshell.

    1. 1*s*
    2. 4*p*
    3. 5*d*
    4. 4*f*

7. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?

8. How many nodes would you expect a 4*p* orbital to have? A 5*s* orbital?

9. A *p* orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of *n*? If an *s* orbital has two nodes, what is the value of *n*?

## Answers

1. Three subshells, with $l = 0$ (*s*), $l = 1$ (*p*), and $l = 2$ (*d*).

2.

3. A *d* subshell has $l = 2$ and contains 5 orbitals.

4.

5.
    1. 2 electrons; 1 orbital
    2. 6 electrons; 3 orbitals
    3. 10 electrons; 5 orbitals
    4. 14 electrons; 7 orbitals

6.

7. A principal shell with $n = 6$ contains six subshells, with $l = 0$, 1, 2, 3, 4, and 5, respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of $l$ for $n = 4$.

8.
9.

## Contributors

- Anonymous

Modified by Joshua Halpern

Imaginary Number Video from IceDave33 on YouTube

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# 6.6: Building Up The Periodic Table

**Learning Objectives**

- To write the electron configuration of any element
- To relate electron configuration to position in the periodic table

Now you can use the information you learned in Section 2.5 to determine the electronic structure of every element in the periodic table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table.All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

## Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers $n$, $l$, and $m_l$. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. We know that the electron cannot be viewed solely as a particle, due to its wavelike properties spinning. Worse, electrons are very weird things, no one for example, has ever been able to measure the radius of an electron, on the atomic scale it behaves as a point, on the atomic scale (a nm). On smaller scales there have been a lot of ideas but no agreement or proof. What is spinning, or how it is spins is a subject of speculation. The behavior of a quantum particle such as the electron cannot be visualized using concepts from our common experience. What is indisputable that electrons do have a magnetic moment which interacts with magnetic fields.This magnetic moment is called electron spinThe magnetic moment that results when an electron spins. Electrons have two possible orientations (spin up and spin down), which are described by a fourth quantum number ($m_s$)..

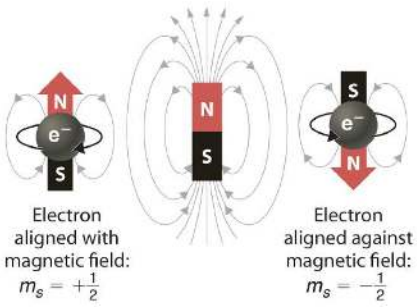



Figure 2.6.1 Electron **Spin** *In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.*

In an external magnetic field, the electron has two possible orientations (Figure 2.6.1). These are described by a fourth quantum number ($m_s$), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript $s$ is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

## The Pauli Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist,Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principleA principle stating that no two electrons in an atom can have the same value of all four quantum numbers.: *No two electrons in an atom can have the same values of all four quantum numbers ($n$, $l$, $m_l$, $m_s$).*

By giving the values of $n$, $l$, and $m_l$, we also specify a particular orbital (e.g., 1$s$ with $n = 1$, $l = 0$, $m_l = 0$). Because $m_s$ has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which, as you learned in Chapter 1 , was originally based on the physical and chemical properties of the known elements.

### Example 2.6.1

List all the allowed combinations of the four quantum numbers ($n$, $l$, $m_l$, $m_s$) for electrons in a 2$p$ orbital and predict the maximum number of electrons the 2$p$ subshell can accommodate.

**Given:** orbital

**Asked for:** allowed quantum numbers and maximum number of electrons in orbital

**Strategy:**

**A** List the quantum numbers ($n$, $l$, $m_l$) that correspond to an $n$ = 2$p$ orbital. List all allowed combinations of ($n$, $l$, $m_l$).

**B** Build on these combinations to list all the allowed combinations of ($n$, $l$, $m_l$, $m_s$).

**C** Add together the number of combinations to predict the maximum number of electrons the 2$p$ subshell can accommodate.

**Solution:**

**A** For a 2$p$ orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \ldots, (l - 1), l$. There are only three possible combinations of ($n$, $l$, $m_l$): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

**B** Because $m_s$ is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of ($n$, $l$, $m_l$, $m_s$): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

**C** Hence the 2$p$ subshell, which consists of three 2$p$ orbitals (2$p_x$, 2$p_y$, and 2$p_z$), can contain a total of six electrons, two in each orbital.

Exercise

List all the allowed combinations of the four quantum numbers ($n$, $l$, $m_l$, $m_s$) for a 6$s$ orbital, and predict the total number of electrons it can contain.

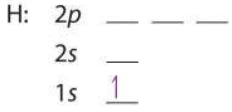
**Answer:** (6, 0, 0, +½), (6, 0, 0, −½); two electrons

## Electron Configurations of the Elements

The electron configurationThe arrangement of an element's electrons in its atomic orbitals. of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

## The Aufbau Principle

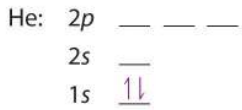
We construct the periodic table by following the aufbau principleThe process used to build up the periodic table by adding protons one by one to the nucleus and adding the corresponding electrons to the lowest-energy orbital available without violating the Pauli exclusion principle. (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 2.5.10 , recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s$ = +½, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s$ = −½. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:




From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number $n$ and their value of $l$ ($s$, $p$, $d$, or $f$), with the number of electrons in the subshell

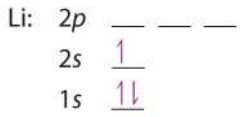
indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy ( Figure 2.5.10 ), and the electron configuration is written as $1s^1$ and read as “one-s-one.”

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



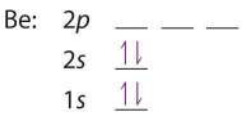

written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle. Remember that because the helium nucleus has a positive charge of +2, the 1s level of helium lies considerably below the 1s level of hydrogen, although for the purposes of building up the periodic table we do not take that into consideration. The orbital diagrams are energy ordered, the levels are in the proper energy order from bottom (most bound) to least, but the energies are not scaled.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired. Figure 2.5.10 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

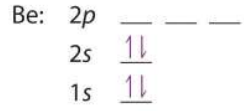



This electron configuration is written as $1s^22s^1$.

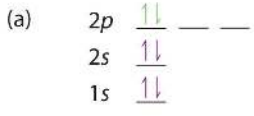
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^22s^2$ electron configuration:



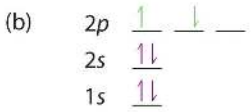

When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Remember that the actual energy difference between the *2s* and *2p* levels is much smaller than that between the *1s* and *2s* levels. Because all three *2p* orbitals are degenerate, it doesn’t matter which one we select. The electron configuration of boron is $1s^22s^22p^1$:



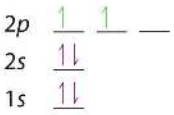

At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?



(b)



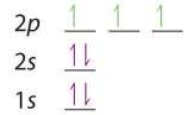

(c)




Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates Hund's ruleA rule stating that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

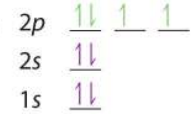
N:




with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

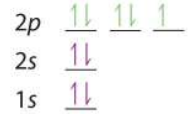
At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the $2p$ orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the $2p$ orbitals are degenerate, it doesn't matter which one has the pair of electrons.

O:



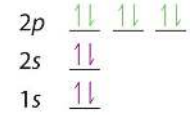

Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:

F:




When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:

Ne:




Notice that for neon, as for helium, all the orbitals through the $2p$ level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

## Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a

noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z$ = 10), so the electron configuration of sodium, with $Z$ = 11, which is $1s^2 2s^2 2p^6 3s^1$, is written as [Ne]$3s^1$:

| | | |
|---|---|---|
| Neon | Z = 10 | $1s^2 2s^2 2p^6$ |
| Sodium | Z = 11 | $1s^2 2s^2 2p^6 \mathbf{3}s^1$ = [Ne]$\mathbf{3}s^1$ |

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the valence electronsElectrons in the outermost shell of an atom.. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

| | |
|---|---|
| Sodium | $1s^2 2s^2 2p^6 3s^1$ = [Ne]$3s^1$ |
| Lithium | $1s^2 2s^1$ = [He]$2s^1$ |

It is readily apparent that both sodium and lithium have one *s* electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3*s* and 3*p* orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration [Ne]$3s^2 3p^6$, corresponding to a filled valence shell.

### Example 2.6.2

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z$ = 15. What is its valence electron configuration?

**Given:** atomic number

**Asked for:** orbital diagram and valence electron configuration for phosphorus

**Strategy:**

**A** Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.

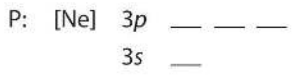
**B** Referring to  Figure 2.5.10 , draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.

**C** Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

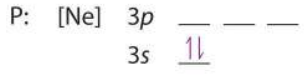
**Solution:**

**A** Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

**B** The additional five electrons are placed in the next available orbitals, which  Figure 2.5.10 tells us are the 3*s* and 3*p* orbitals:




Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:




Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:

P: [Ne] 3*p* ↑ ↑ ↑
3*s* ↑↓

The electron configuration is [Ne]$3s^2 3p^3$.

**C** We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

Exercise

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z$ = 17. What is its valence electron configuration?

**Answer:** [Ne]$3s^2 3p^5$; $3s^2 3p^5$

The general order in which orbitals are filled is depicted in Figure 2.6.2 . Subshells corresponding to each value of $n$ are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton ($Z$ = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

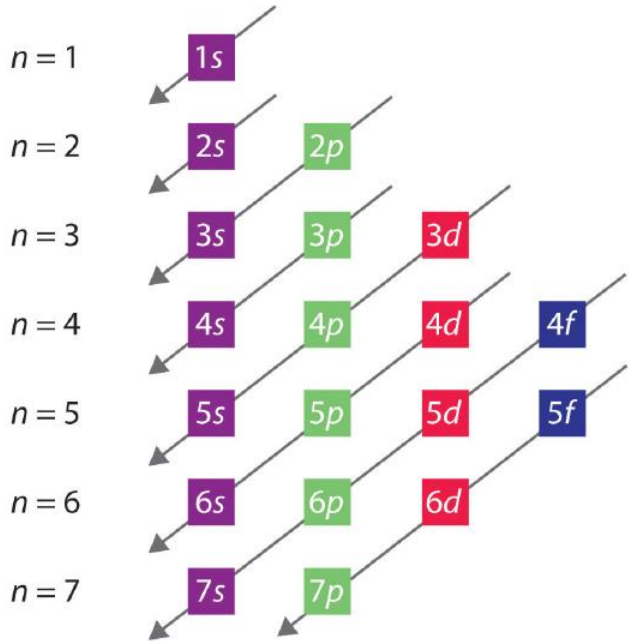



Figure 2.6.2 Predicting the Order in Which Orbitals Are Filled in Multielectron **Atoms** *If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.*

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next (and last known) noble gas, radon ($Z$ = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

### Example 2.6.3

Write the electron configuration of mercury ($Z = 80$), showing all the inner orbitals.

**Given:** atomic number

**Asked for:** complete electron configuration

**Strategy:**

Using the orbital diagram in Figure 2.6.2 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

**Solution:**

By placing the electrons in orbitals following the order shown in Figure 2.6.2 and using the periodic table as a guide, we obtain

| | | |
|---|---|---|
| $1s^2$ | row 1 | 2 electrons |
| $2s^2 2p^6$ | row 2 | 8 electrons |
| $3s^2 3p^6$ | row 3 | 8 electrons |
| $4s^2 3d^{10} 4p^6$ | row 4 | 18 electrons |
| $5s^2 4d^{10} 5p^6$ | row 5 | 18 electrons |
| | row 1–5 | 54 electrons |

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure 2.6.3 , we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = \text{Hg} = [\text{Xe}] 6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise

Although element 114 is not stable enough to occur in nature, two isotopes of element 114 were created for the first time in a nuclear reactor in 1999 by a team of Russian and American scientists. Write the complete electron configuration for element 114.

**Answer:** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure 2.6.4 , which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 2.6.2 . Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is $[\text{Ar}] 4s^1 3d^5$ rather than the predicted $[\text{Ar}] 4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[\text{Ar}] 4s^1 3d^{10}$ instead of $[\text{Ar}] s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled ($ns^1$, $np^3$, $nd^5$, $nf^7$) or filled ($ns^2$, $np^6$, $nd^{10}$, $nf^{14}$) subshell. Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to some of the additional anomalies indicated in Figure 2.6.5 For example, cerium has an electron configuration of $[\text{Xe}] 6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

### Note the Pattern

Additional stability is associated with half-filled or filled subshells.

## Blocks in the Periodic Table

The electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a

particular order. As a result, the periodic table can be divided into “blocks” corresponding to the type of subshell that is being filled, as illustrated in Figure 2.6.4 . For example, the two columns on the left, known as the *s* blockThe elements in the left two columns of the periodic table in which the *ns* orbital is being filled., consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* blockThe elements in the six columns on the right of the periodic table in which the *np* orbitals are being filled.. In between are the 10 columns of the *d* blockThe elements in the periodic table in which the $(n - 1)d$ orbitals are being filled., elements in which the $(n - 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* blockThe elements in the periodic table in which the $(n - 2)f$ orbitals are being filled., elements in which the $(n - 2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n - 1)d$, and 14 for $(n - 2)f$. Within each column, each element has the same valence electron configuration—for example, $ns^1$ (group 1) or $ns^2np^1$ (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

## Note the Pattern

Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s* block, 6 columns in the *p* block, 10 columns in the *d* block, and 14 columns in the *f* block.

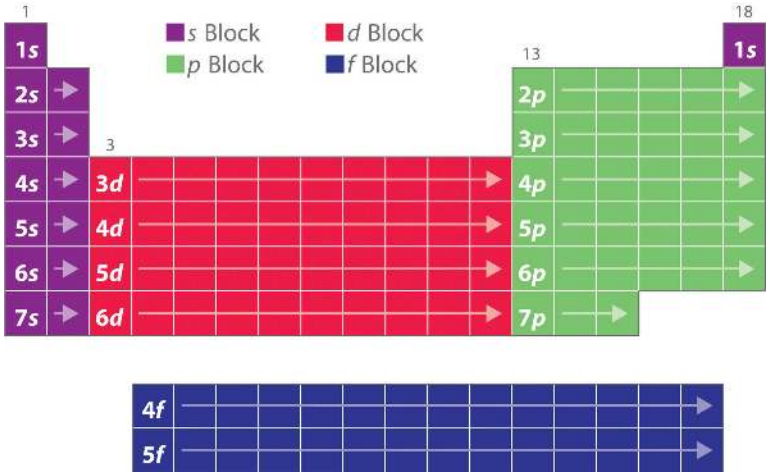



Figure 2.6.3 The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element

The electron configurations of the elements are in Figure 2.6.5 .

There is an alternate form, which integrates the f orbitals into the main table

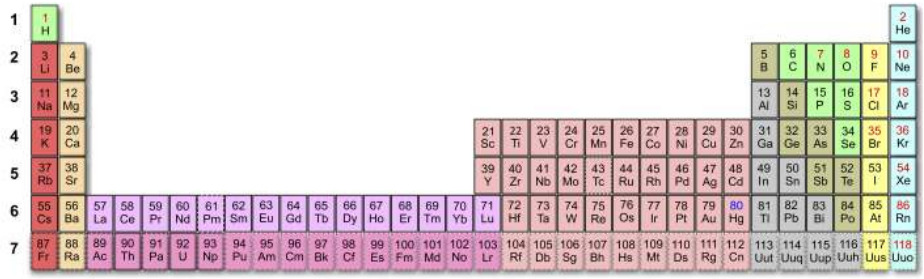


**Figure 2.6.4 "An Alternate Form of the Periodic Table** *This wide form of the periodic table shows how the 4f/5f orbitals fit between the 6s/7s and 5d/6d orbitals*

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ($[He]2s^1$) and the other elements in the first column. Although helium, with a filled *ns* subshell, should be similar chemically to other elements with an $ns^2$ electron configuration, the closed principal shell dominates its

chemistry, justifying its placement above neon on the right. In Chapter 3, we will examine how electron configurations affect the properties and reactivity of the elements.

| Atomic number | Symbol | Electron configuration | Atomic number | Symbol | Electron configuration | Atomic number | Symbol | Electron configuration |
|---|---|---|---|---|---|---|---|---|
| 1 | H | $1s^1$ | 37 | Rb | [Kr]$5s^1$ | 73 | Ta | [Xe]$6s^2 4f^{14} 5d^3$ |
| 2 | He | $1s^2$ | 38 | Sr | [Kr]$5s^2$ | 74 | W | [Xe]$6s^2 4f^{14} 5d^4$ |
| 3 | Li | [He]$2s^1$ | 39 | Y | [Kr]$5s^2 4d^1$ | 75 | Re | [Xe]$6s^2 4f^{14} 5d^5$ |
| 4 | Be | [He]$2s^2$ | 40 | Zr | [Kr]$5s^2 4d^2$ | 76 | Os | [Xe]$6s^2 4f^{14} 5d^6$ |
| 5 | B | [He]$2s^2 2p^1$ | 41 | Nb | [Kr]$5s^1 4d^4$ | 77 | Ir | [Xe]$6s^2 4f^{14} 5d^7$ |
| 6 | C | [He]$2s^2 2p^2$ | 42 | Mo | [Kr]$5s^1 4d^5$ | 78 | Pt | [Xe]$6s^1 4f^{14} 5d^9$ |
| 7 | N | [He]$2s^2 2p^3$ | 43 | Tc | [Kr]$5s^2 4d^5$ | 79 | Au | [Xe]$6s^1 4f^{14} 5d^{10}$ |
| 8 | O | [He]$2s^2 2p^4$ | 44 | Ru | [Kr]$5s^1 4d^7$ | 80 | Hg | [Xe]$6s^2 4f^{14} 5d^{10}$ |
| 9 | F | [He]$2s^2 2p^5$ | 45 | Rh | [Kr]$5s^1 4d^8$ | 81 | Tl | [Xe]$6s^2 4f^{14} 5d^{10} 6p^1$ |
| 10 | Ne | [He]$2s^2 2p^6$ | 46 | Pd | [Kr]$4d^{10}$ | 82 | Pb | [Xe]$6s^2 4f^{14} 5d^{10} 6p^2$ |
| 11 | Na | [Ne]$3s^1$ | 47 | Ag | [Kr]$5s^1 4d^{10}$ | 83 | Bi | [Xe]$6s^2 4f^{14} 5d^{10} 6p^3$ |
| 12 | Mg | [Ne]$3s^2$ | 48 | Cd | [Kr]$5s^2 4d^{10}$ | 84 | Po | [Xe]$6s^2 4f^{14} 5d^{10} 6p^4$ |
| 13 | Al | [Ne]$3s^2 3p^1$ | 49 | In | [Kr]$5s^1 4d^{10} 5p^1$ | 85 | At | [Xe]$6s^2 4f^{14} 5d^{10} 6p^5$ |
| 14 | Si | [Ne]$3s^2 3p^2$ | 50 | Sn | [Kr]$5s^1 4d^{10} 5p^2$ | 86 | Rn | [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ |
| 15 | P | [Ne]$3s^2 3p^3$ | 51 | Sb | [Kr]$5s^1 4d^{10} 5p^3$ | 87 | Fr | [Rn]$7s^1$ |
| 16 | S | [Ne]$3s^2 3p^4$ | 52 | Te | [Kr]$5s^1 4d^{10} 5p^4$ | 88 | Ra | [Rn]$7s^2$ |
| 17 | Cl | [Ne]$3s^2 3p^5$ | 53 | I | [Kr]$5s^1 4d^{10} 5p^5$ | 89 | Ac | [Rn]$7s^2 6d^1$ |
| 18 | Ar | [Ne]$3s^2 3p^6$ | 54 | Xe | [Kr]$5s^1 4d^{10} 5p^6$ | 90 | Th | [Rn]$7s^2 6d^2$ |
| 19 | K | [Ar]$4s^1$ | 55 | Cs | [Xe]$6s^1$ | 91 | Pa | [Rn]$7s^2 5f^2 6d^1$ |
| 20 | Ca | [Ar]$4s^2$ | 56 | Ba | [Xe]$6s^2$ | 92 | U | [Rn]$7s^2 5f^3 6d^1$ |
| 21 | Sc | [Ar]$4s^2 3d^1$ | 57 | La | [Xe]$6s^2 5d^1$ | 93 | Np | [Rn]$7s^2 5f^4 6d^1$ |
| 22 | Ti | [Ar]$4s^2 3d^2$ | 58 | Ce | [Xe]$6s^2 4f^1 5d^1$ | 94 | Pu | [Rn]$7s^2 5f^6$ |
| 23 | V | [Ar]$4s^2 3d^3$ | 59 | Pr | [Xe]$6s^2 4f^3$ | 95 | Am | [Rn]$7s^2 5f^7$ |
| 24 | Cr | [Ar]$4s^1 3d^5$ | 60 | Nd | [Xe]$6s^2 4f^4$ | 96 | Cm | [Rn]$7s^2 5f^7 6d^1$ |
| 25 | Mn | [Ar]$4s^2 3d^5$ | 61 | Pm | [Xe]$6s^2 4f^5$ | 97 | Bk | [Rn]$7s^2 5f^9$ |
| 26 | Fe | [Ar]$4s^2 3d^6$ | 62 | Sm | [Xe]$6s^2 4f^6$ | 98 | Cf | [Rn]$7s^2 5f^{10}$ |
| 27 | Co | [Ar]$4s^2 3d^7$ | 63 | Eu | [Xe]$6s^2 4f^7$ | 99 | Es | [Rn]$7s^2 5f^{11}$ |
| 28 | Ni | [Ar]$4s^2 3d^8$ | 64 | Gd | [Xe]$6s^2 4f^7 5d^1$ | 100 | Fm | [Rn]$7s^2 5f^{12}$ |
| 29 | Cu | [Ar]$4s^1 3d^{10}$ | 65 | Tb | [Xe]$6s^2 4f^9$ | 101 | Md | [Rn]$7s^2 5f^{13}$ |
| 30 | Zn | [Ar]$4s^2 3d^{10}$ | 66 | Dy | [Xe]$6s^2 4f^{10}$ | 102 | No | [Rn]$7s^2 5f^{14}$ |
| 31 | Ga | [Ar]$4s^2 3d^{10} 4p^1$ | 67 | Ho | [Xe]$6s^2 4f^{11}$ | 103 | Lr | [Rn]$7s^2 5f^{14} 6d^1$ |
| 32 | Ge | [Ar]$4s^2 3d^{10} 4p^2$ | 68 | Er | [Xe]$6s^2 4f^{12}$ | 104 | Rf | [Rn]$7s^2 5f^{14} 6d^2$ |
| 33 | As | [Ar]$4s^2 3d^{10} 4p^3$ | 69 | Tm | [Xe]$6s^2 4f^{13}$ | 105 | Db | [Rn]$7s^2 5f^{14} 6d^3$ |
| 34 | Se | [Ar]$4s^2 3d^{10} 4p^4$ | 70 | Yb | [Xe]$6s^2 4f^{14}$ | 106 | Sg | [Rn]$7s^2 5f^{14} 6d^4$ |
| 35 | Br | [Ar]$4s^2 3d^{10} 4p^5$ | 71 | Lu | [Xe]$6s^2 4f^{14} 5d^1$ | 107 | Bh | [Rn]$7s^2 5f^{14} 6d^5$ |
| 36 | Kr | [Ar]$4s^2 3d^{10} 4p^6$ | 72 | Hf | [Xe]$6s^2 4f^{14} 5d^2$ | 108 | Hs | [Rn]$7s^2 5f^{14} 6d^6$ |
| | | | | | | 109 | Mt | [Rn]$7s^2 5f^{14} 6d^7$ |
| | | | | | | 110 | Ds | [Rn]$7s^1 5f^{14} 6d^9$ |
| | | | | | | 111 | Rg | [Rn]$7s^1 5f^{14} 6d^{10}$ |

Figure 2.6.5 Electron Configurations of the Elements *The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.*

## Example 2.6.4

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

**Given:** series of elements

**Asked for:** valence electron configurations

**Strategy:**

**A** Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.

**B** Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

**Solution:**

**A** The group 2 elements are in the *s* block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its valence shell is $n = 2$.

**B** Thus beryllium has an [He]$s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: [Ne]$s^2$. By extrapolation, we expect all the group 2 elements to have an $ns^2$ electron configuration.

Exercise

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

**Answer:** All have an $ns^2np^5$ electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n - 1)d^{10}$ subshells, as well as an $(n - 2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.

## Summary

In addition to the three quantum numbers ($n$, $l$, $m_l$) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number ($m_s$), which can have values of +½ or −½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin). Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**. The arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals to produce the distinctive chemical properties of the elements in the *s* **block**, *p* **block**, *d* **block**, and *f* **block**, respectively.

## Key Takeaway

- The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell.

## Conceptual Problems

1. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? What does the specified wave function describe?
2. List two pieces of evidence to support the statement that electrons have a spin.
3. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Which quantum number distinguishes the horizontal rows?
4. Identify the element with each ground state electron configuration.
    1. [He]$2s^2 2p^3$
    2. [Ar]$4s^2 3d^1$
    3. [Kr]$5s^2 4d^{10} 5p^3$
    4. [Xe]$6s^2 4f^6$
5. Identify the element with each ground state electron configuration.
    1. [He]$2s^2 2p^1$
    2. [Ar]$4s^2 3d^8$
    3. [Kr]$5s^2 4d^{10} 5p^4$
    4. [Xe]$6s^2$
6. Propose an explanation as to why the noble gases are inert.

## Numerical Problems

1. How many magnetic quantum numbers are possible for a 4*p* subshell? A 3*d* subshell? How many orbitals are in these subshells?
2. How many magnetic quantum numbers are possible for a 6*s* subshell? A 4*f* subshell? How many orbitals does each subshell contain?
3. If $l = 2$ and $m_l = 2$, give all the allowed combinations of the four quantum numbers ($n$, $l$, $m_l$, $m_s$) for electrons in the corresponding 3*d* subshell.
4. Give all the allowed combinations of the four quantum numbers ($n$, $l$, $m_l$, $m_s$) for electrons in a 4*d* subshell. How many electrons can the 4*d* orbital accommodate? How would this differ from a situation in which there were only three quantum numbers ($n$, $l$, $m$)?
5. Given the following sets of quantum numbers ($n$, $l$, $m_l$, $m_s$), identify each principal shell and subshell.
    1. 1, 0, 0, ½
    2. 2, 1, 0, ½
    3. 3, 2, 0, ½
    4. 4, 3, 3, ½
6. Is each set of quantum numbers allowed? Explain your answers.
    1. $n = 2$; $l = 1$; $m_l = 2$; $m_s = +½$
    2. $n = 3$, $l = 0$; $m_l = −1$; $m_s = −½$
    3. $n = 2$; $l = 2$; $m_l = 1$; $m_s = +½$
    4. $n = 3$; $l = 2$; $m_l = 2$; $m_s = +½$
7. List the set of quantum numbers for each electron in the valence shell of each element.
    1. beryllium
    2. xenon
    3. lithium
    4. fluorine
8. List the set of quantum numbers for each electron in the valence shell of each element.
    1. carbon
    2. magnesium
    3. bromine
    4. sulfur
9. Sketch the shape of the periodic table if there were three possible values of $m_s$ for each electron (+½, −½, and 0); assume that the Pauli principle is still valid.
10. Predict the shape of the periodic table if eight electrons could occupy the *p* subshell.
11. If the electron could only have spin +½, what would the periodic table look like?
12. If three electrons could occupy each *s* orbital, what would be the electron configuration of each species?
    1. sodium
    2. titanium
    3. fluorine
    4. calcium
13. If Hund's rule were not followed and maximum pairing occurred, how many unpaired electrons would each species have? How do these numbers compare with the number found using Hund's rule?
    1. phosphorus
    2. iodine
    3. manganese

14. Write the electron configuration for each element in the ground state.
    1. aluminum
    2. calcium
    3. sulfur
    4. tin
    5. nickel
    6. tungsten
    7. neodymium
    8. americium
15. Write the electron configuration for each element in the ground state.
    1. boron
    2. rubidium
    3. bromine
    4. germanium
    5. vanadium
    6. palladium
    7. bismuth
    8. europium
16. Give the complete electron configuration for each element.
    1. magnesium
    2. potassium
    3. titanium
    4. selenium
    5. iodine
    6. uranium
    7. germanium
17. Give the complete electron configuration for each element.
    1. tin
    2. copper
    3. fluorine
    4. hydrogen
    5. thorium
    6. yttrium
    7. bismuth
18. Write the valence electron configuration for each element:
    1. samarium
    2. praseodymium
    3. boron
    4. cobalt
19. Using the Pauli exclusion principle and Hund’s rule, draw valence orbital diagrams for each element.
    1. barium
    2. neodymium
    3. iodine
20. Using the Pauli exclusion principle and Hund’s rule, draw valence orbital diagrams for each element.
    1. chlorine

2. silicon
3. scandium

21. How many unpaired electrons does each species contain?

    1. lead
    2. cesium
    3. copper
    4. silicon
    5. selenium

22. How many unpaired electrons does each species contain?

    1. helium
    2. oxygen
    3. bismuth
    4. silver
    5. boron

23. For each element, give the complete electron configuration, draw the valence electron configuration, and give the number of unpaired electrons present.

    1. lithium
    2. magnesium
    3. silicon
    4. cesium
    5. lead

24. Use an orbital diagram to illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule for each element.

    1. carbon
    2. sulfur

## Answers

1. For a 4*p* subshell, $n = 4$ and $l = 1$. The allowed values of the magnetic quantum number, $ml$, are therefore +1, 0, −1, corresponding to three 4*p* orbitals. For a 3*d* subshell, $n = 3$ and $l = 2$. The allowed values of the magnetic quantum number, $ml$, are therefore +2, +1, 0, −1, −2, corresponding to five 3*d* orbitals.
2. 
3. $n = 3$, $l = 2$, $ml = 2$, $m_s = 1/2$; $n = 3$, $l = 2$, $m_l = 2$, $m_s = -1/2$
4. 
5. 
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24.

## Contributors

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Modified by Joshua Halpern

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# 6.7: Electronic Structure of the Transition Metals

**Learning Objectives**

- To write the electron configuration of the transition metals.
- To understand the basis for the exceptions to the normal order of filling.

Now you can use the information you learned in Section 2.5 to determine the electronic structure of every element in the periodic table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table. Well almost, but the exceptions are instructional.

Adding a proton and an electron to form the next atom results in small changes in the energy levels relative to each other but the order remains the same, at least until we get to the *d* levels, where in some atoms the relative energies of the *ns* and the *(n-1)d* orbitals shifts. In the fourth period, this happens for Cr and Cu, which, instead of having two electrons in the *4s* orbital have only one. The first three elements in the d block of the fourth period sequentially have one more d electron than the last. In agreement with Hund's rules each of these is added to a different d orbital with parallel spins.

For Cr, something different happens, of the six electrons, five are found in the *4d* level and only one in the *4s*. Electron repulsion and favoring parallel spins moves the *3d* level below the *4s* when there are 6 electrons. The normal pattern resumes with Mn (manganese).

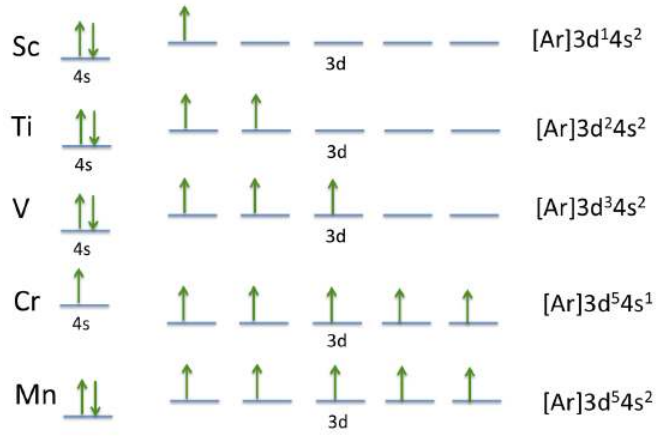



**Figure 2.7.1 The electronic configurations of the first five fourth period transition metals** *Notice how the relative positions of the 4s and 3d orbitals move relative to each other as more electrons are added.*

If we continue on to Zn, the "exception" repeats itself with Cu, where there are now 10 electrons in the *3d* level and only one in the *4s*.

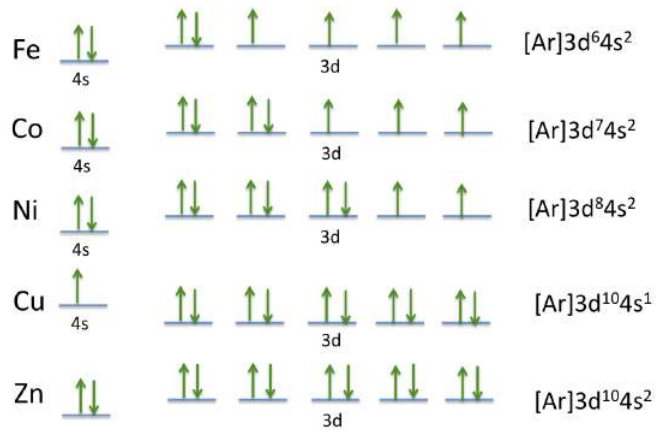



Figure 2.7.2 The electronic configurations of the last five fourth period transition metals

We can look at the electron configurations of the rest of the *d* block elements.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 21 Sc $[Ar]3d^14s^2$ | 22 Ti $[Ar]3d^24s^2$ | 23 V $[Ar]3d^34s^2$ | 24 Cr $[Ar]\ 3d^54s^1$ | 25 Mn $[Ar]3d^54s^2$ | 26 Fe $[Ar]3d^64s^2$ | 27 Co $[Ar]3d^74s^2$ | 28 N $[Ar]3d^84s^2$ | 29 Cu $[Ar]3d^{10}4s^1$ | 30 Zn $[Ar]3d^{10}4s^2$ |
| 39 Y $[Kr]4d^15s^2$ | 40 Zr $[Kr]4d^25s^2$ | 41 Nb $[Kr]4d^35s^2$ | 42 Mo $[Kr]4d^55s^1$ | 43 Tc $[Kr]4d^55s^2$ | 44 Ru $[Kr]4d^75s^1$ | 45 Rh $[Kr]4d^85s^1$ | 46 Pd $[Kr]4d^{10}$ | 47 Ag $[Kr]4d^{10}5s^1$ | 48 Cd $[Kr]4d^{10}5s^2$ |
| 57 La $[Xe]6s^25d^1$ | 72 Hf $[Xe]5d^26s^2$ | 73 Ta $[Xe]5d^36s^2$ | 74 W $[Xe]5d^46s^2$ | 75 Re $[Xe]5d^56s^2$ | 76 Os $[Xe]5d^66s^2$ | 77 Ir $[Xe]5d^76s^2$ | 78 Pt $[Xe]5d^96s^1$ | 79 Au $[Xe]5d^{10}6s^1$ | 80 Hg $[Xe]5d^{10}6s^2$ |
| | | | | | | | | | |

Figure 2.7.3 The electronic configurations of the transition metals. Only the ns and (n-1)d electrons have been shown to save space. The 14 electrons in the atoms from Hf to Hg have not been written in. *The electron configuration of Mo (molybdenum) is similar to that of Cr, and both are shown in green. Those metals shown in blue, with the exception of Pd, paladium, have only one ns electron. Pd has none. Cu, Ag, Au and Pd have ten electrons in the (n-1)d orbitals. These metals are all very soft, fairly unreactive, rare, and with the exception of Cu used in jewelry.*

The transition metals, as a general rule, have similar properties. The reason for this is that the extent of the orbitals from the nucleus depends on the principal quantum numbers. Thus, the orbitals of the *ns* electrons extend further out than those of the *(n-1) d* electrons in the same periods, and therefore are more available for bonding and reactions. As other atoms and molecules approach the metal atoms, the *ns* electrons are the ones that are first affected.

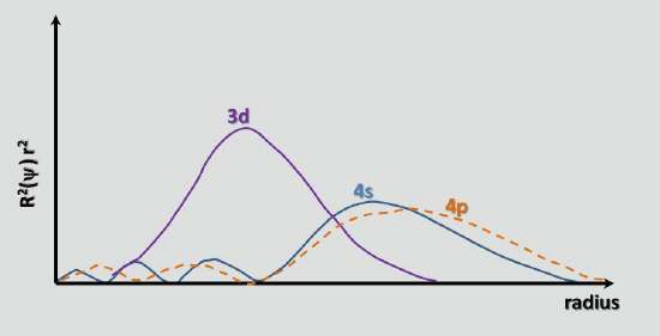



**Figure 2.7.4 The Probability Density of the 4s, 4p and 3d Electrons as a Function of Radial Distance from the Nucleus** *The ns orbitals of the transition metals extend further from the nucleus than those of the (n-1)d orbitals, making them more available for bonding and reactions. This is illustrated here for the fourth period. Similarly the f orbitals of the rare earths and the lanthanides are packed in closer to the nucleus than those of the s and p orbitals in the same periods.*

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# CHAPTER OVERVIEW

## 7: The Periodic Table and Periodic Trends


7.1: The History of the Periodic Table

7.2: Sizes of Atoms and Ions

7.3: The Chemical Families

7.4: Trace Elements in Biological Systems


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# 7.1: The History of the Periodic Table

**Learning Objectives**

- To become familiar with the history of the periodic table

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triadsA set of three elements that have similar properties., sets of three elements that have similar properties—for example, chlorine, bromine, and iodine; or copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the periodic table—the *d* block in particular—contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur, selenium, and tellurium in group 16 or aluminum, gallium, and indium in group 13, also have remarkably similar chemistry.

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 3.1.1 ). Newlands therefore suggested that the elements could be classified into octaves. He described octaves as a group of seven elements, which correspond to the horizontal rows in the main groups of today's periodic table. There were seven elements because the noble gases were not known at the time. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of $ns^2np^6$ subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

### John Newlands (1838–1898)

Newlands noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.

| No. | No. | No. | No. | No. | No. | No. | No. |
|---|---|---|---|---|---|---|---|
| H 1 | F 8 | Cl 15 | Co & Ni 22 | Br 29 | Pd 36 | I 42 | Pt & Ir 50 |
| Li 2 | Na 9 | K 16 | Cu 23 | Rb 30 | Ag 37 | Cs 44 | Tl 51 |
| G 3 | Mg 10 | Ca 17 | Zn 25 | Sr 31 | Bd [sic-Cd] 38 | Ba & V 45 | Pb 54 |
| Bo 4 | Al 11 | Cr 19 | Y 24 | Ce & La 33 | U 40 | Ta 46 | Th 56 |
| C 5 | Si 12 | Ti 18 | In 26 | Zr 32 | Sn 39 | W 47 | Hg 52 |
| N 6 | P 13 | Mn 20 | As 27 | Di & Mo 34 | Sb 41 | Nb 48 | Bi 55 |
| O 7 | S 14 | Fe 21 | Se 28 | Ro & Ru 35 | Te 43 | Au 49 | Os 51 |

**NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.**

Figure 3.1.1 The Arrangement of the Elements into Octaves as Proposed by Newlands *The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal Chemical News in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the Law of Octaves. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."*

The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as "atomic volume" (Figure

3.1.2 ), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density, (measured in cubic centimeters per mole):

$$\frac{molar\ mass\ \left(\not{g}/mol\right)}{density\left(\not{g}/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{3.1.1}$$

As shown in Figure 3.1.2 , the alkali metals have the highest molar volumes of the solid elements. In Meyer's plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

### Dimitri Mendeleev (1834–1907)

When his family's glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students. In addition to the periodic table, another of Mendeleev's contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

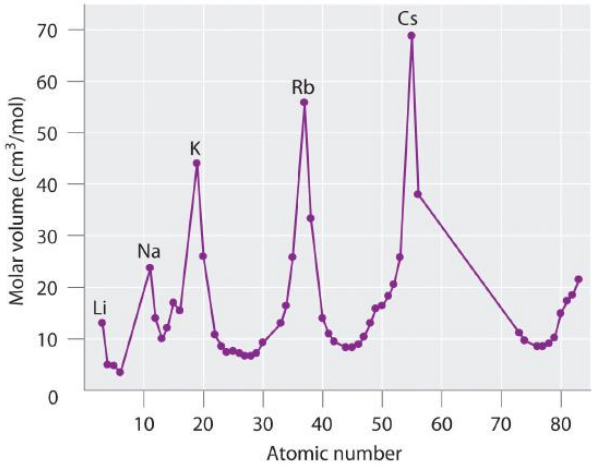
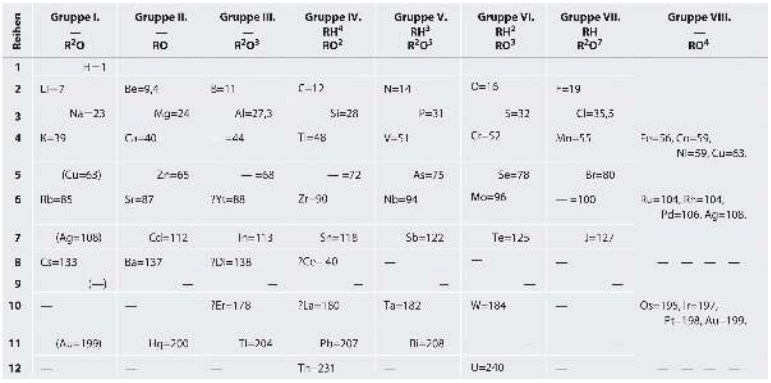



Figure 3.1.2 Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of **1870.** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

## Mendeleev's Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure 3.1.3 ), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.



| Reihen | Gruppe I. — $R^2O$ | Gruppe II. — RO | Gruppe III. — $R^2O^3$ | Gruppe IV. $RH^4$ $RO^2$ | Gruppe V. $RH^3$ $R^2O^5$ | Gruppe VI. $RH^2$ $RO^3$ | Gruppe VII. RH $R^2O^7$ | Gruppe VIII. — $RO^4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H=1 | | | | | | | |
| 2 | Li=7 | Be=9,4 | B=11 | C=12 | N=14 | O=16 | F=19 | |
| 3 | Na=23 | Mg=24 | Al=27,3 | Si=28 | P=31 | S=32 | Cl=35,5 | |
| 4 | K=39 | Ca=40 | =44 | Ti=48 | V=51 | Cr=52 | Mn=55 | Fe=56, Co=59, Ni=59, Cu=63. |
| 5 | (Cu=63) | Zn=65 | —=68 | —=72 | As=75 | Se=78 | Br=80 | |
| 6 | Rb=85 | Sr=87 | ?Yt=88 | Zr=90 | Nb=94 | Mo=96 | —=100 | Ru=104, Rh=104, Pd=106, Ag=108. |
| 7 | (Ag=108) | Cd=112 | In=113 | Sn=118 | Sb=122 | Te=125 | J=127 | |
| 8 | Cs=133 | Ba=137 | ?Di=138 | ?Ce=140 | — | — | — | — — — — |
| 9 | (—) | — | — | — | — | — | — | |
| 10 | — | — | ?Er=178 | ?La=180 | Ta=182 | W=184 | — | Os=195, Ir=197, Pt=198, Au=199. |
| 11 | (Au=199) | Hg=200 | Tl=204 | Pb=207 | Bi=208 | | | |
| 12 | — | — | — | Th=231 | — | U=240 | — | — — — — |

Figure 3.1.3 Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in **1872.** *The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.*

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium, Li, sodium, Na, and potassium form compounds with one atom of oxygen. In Group VII, one atom of fluorine, F, chlorine, Cl, and bromine, Br, react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 3.1.1 ). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.




**Table 3.1.1 Comparison of the Properties Predicted by Mendeleev in 1869 for *eka*-Aluminum and *eka*-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)**

| Property | *eka*-Aluminum (predicted) | Gallium (observed) | *eka*-Silicon (predicted) | Germanium (observed) |
|---|---|---|---|---|
| atomic mass | 68 | 69.723 | 72 | 72.64 |
| element | metal | metal | dirty-gray metal | gray-white metal |
| | low mp* | mp = 29.8°C | high mp | mp = 938°C |
| | $d$ = 5.9 g/cm$^3$ | $d$ = 5.91 g/cm$^3$ | $d$ = 5.5 g/cm$^3$ | $d$ = 5.323 g/cm$^3$ |
| oxide | $E_2O_3$ | $Ga_2O_3$ | $EO_2$ | $GeO_2$ |
| | $d$ = 5.5 g/cm$^3$ | $d$ = 6.0 g/cm$^3$ | $d$ = 4.7 g/cm$^3$ | $d$ = 4.25 g/cm$^3$ |
| chloride | $ECl_3$ | $GaCl_3$ | $ECl_4$ | $GeCl_4$ |
| | volatile | mp = 78°C<br>bp* = 201°C | bp < 100°C | bp = 87°C |

*mp = melting point; bp = boiling point.

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really $In_2O_3$ rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

One group of elements that absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

## The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number $Z$, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium ($Z$ = 43), discovered in 1937; promethium ($Z$ = 61), discovered in 1945; and rhenium ($Z$ = 75), discovered in 1925.

### H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.

### Example 3.1.1

Before its discovery in 1999, some theoreticians believed that an element with a $Z$ of 114 existed in nature. Use Mendeleev's reasoning to name element 114 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 114.

**Given:** atomic number

**Asked for:** name using prefix *eka*-

**Strategy:**

**A** Using the periodic table locate the $n = 7$ row. Identify the location of the unknown element with $Z = 114$; then identify the known element that is directly above this location.

**B** Name the unknown element by using the prefix *eka*- before the name of the known element.

**Solution:**

**A** The $n = 7$ row can be filled in by assuming the existence of elements with atomic numbers greater than 112, which is underneath mercury (Hg). Counting three boxes to the right gives element 114, which lies directly below lead (Pb). **B** If Mendeleev were alive today, he would call element 114 *eka*-lead.

Exercise

Use Mendeleev's reasoning to name element 112 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 112.

**Answer:** *eka*-mercury

## Summary

The periodic table arranges the elements according to their electron configurations, such that elements in the same column have the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties. The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, who both focused on the relationship between atomic mass and chemical properties. Meyer arranged the elements by their atomic volume, which today is equivalent to the **molar volume**, defined as molar mass divided by molar density. The correlation with the electronic structure of atoms was made when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

## Key Takeaway

- The elements in the periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.

## Conceptual Problems

1. Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.
2. Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?
3. How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
4. The *eka*- naming scheme devised by Mendeleev was used to describe undiscovered elements.
    1. Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
    2. Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

## Numerical Problem

1. Based on the data given, complete the table.

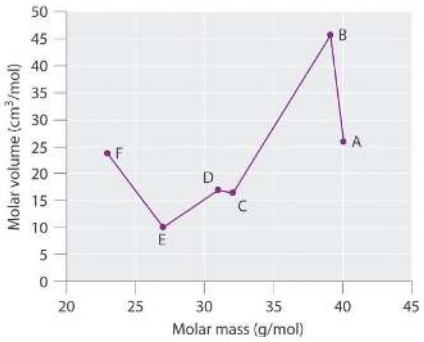
| Species | Molar Mass (g/mol) | Density (g/cm$^3$) | Molar Volume (cm$^3$/mol) |
|---|---|---|---|
| A | 40.078 | | 25.85 |
| B | 39.09 | 0.856 | |
| C | 32.065 | | 16.35 |
| D | | 1.823 | 16.98 |
| E | 26.98 | | 9.992 |
| F | 22.98 | 0.968 | |

Plot molar volume versus molar mass for these substances. According to Meyer, which would be considered metals and which would be considered nonmetals?

## Answer

1.

| Species | Molar Mass (g/mol) | Density (g/cm$^3$) | Molar Volume (cm$^3$/mol) |
|---|---|---|---|
| A | **40.078** | 1.550 | **25.85** |
| B | **39.09** | **0.856** | 45.67 |
| C | **32.065** | 1.961 | **16.35** |
| D | 30.95 | **1.823** | **16.98** |
| E | **26.98** | 2.700 | **9.992** |
| F | **22.98** | **0.968** | 23.7 |




Meyer found that the alkali metals had the highest molar volumes, and that molar volumes decreased steadily with increasing atomic mass, then leveled off, and finally rose again. The elements located on the rising portion of a plot of molar volume versus molar mass were typically nonmetals. If we look at the plot of the data in the table, we can immediately identify those elements with the largest molar volumes (A, B, F) as metals located on the left side of the periodic table. The element with the smallest molar volume (E) is aluminum. The plot shows that the subsequent elements (C, D) have molar volumes that are larger than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

## Contributors

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Genius of Mendelev by TED Ed on YouTube

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# 7.2: Sizes of Atoms and Ions

**Learning Objectives**

- To understand periodic trends in atomic radii.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

## Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 3.2.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

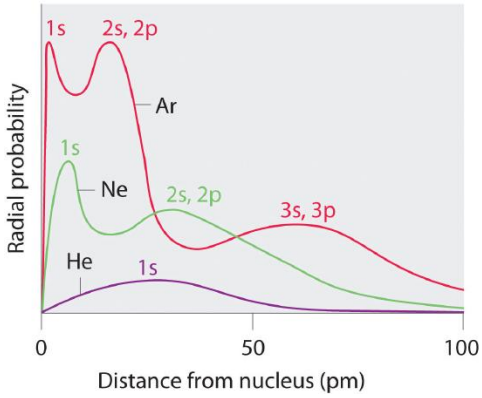



Figure 3.2.1 Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and **Ar.** *In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm.*

Figure 3.2.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1$, 2, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of $n$. Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1*s* orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure 3.2.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic $Cl_2$ molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius ($r_{cov}$), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (part (a) in Figure 3.2.2). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 Å = 1 \times 10^{-10}$ m = 100 pm.

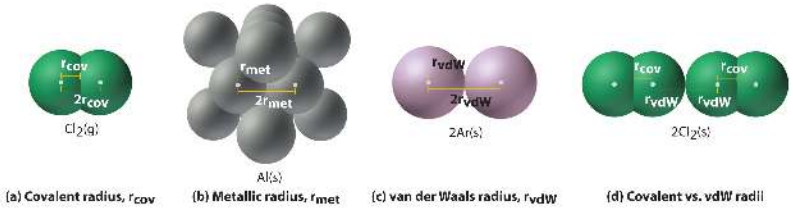



Figure 3.2.2 Definitions of the Atomic Radius. *(a) The covalent atomic radius, $r_{cov}$, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as $Cl_2$. (b) The metallic atomic radius, $r_{met}$, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, $r_{vdW}$, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of $Cl_2$ is the distance between the two chlorine atoms in a single molecule of $Cl_2$. The van der Waals radius is the distance between chlorine nuclei in two different but touching $Cl_2$ molecules. Which do you think is larger? Why?*

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds.A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius($r_{met}$) is defined as half the distance between the nuclei of two adjacent metal atoms (part (b) in Figure 3.2.2). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius ($r_{vdW}$), which is half the internuclear distance between two nonbonded atoms in the solid (part (c) in Figure 3.2.2 ). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a $Cl_2$ molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_2(s)$ at low temperatures). These radii are generally not the same (part (d) in Figure 3.2.2 ).

## Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions described in Chapter 2. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 3.2.3). In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 3.2.4).

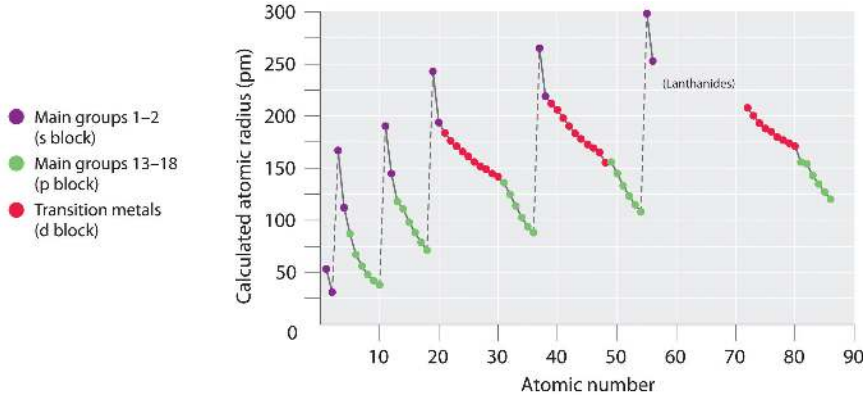



Figure 3.1.2 )—a variation of Meyer's early plot.

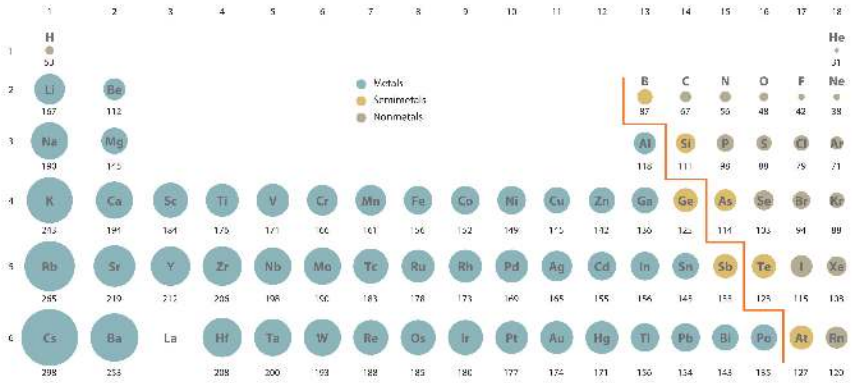



Figure 3.2.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block **Elements.** *The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties. Visit the site.*

## Note the Pattern

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

Trends in atomic size result from differences in the **effective nuclear charges ($Z_{eff}$)** experienced by electrons in the outermost orbitals of the elements. As we described in Chapter 2, for all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of $Z_{eff}$ = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.

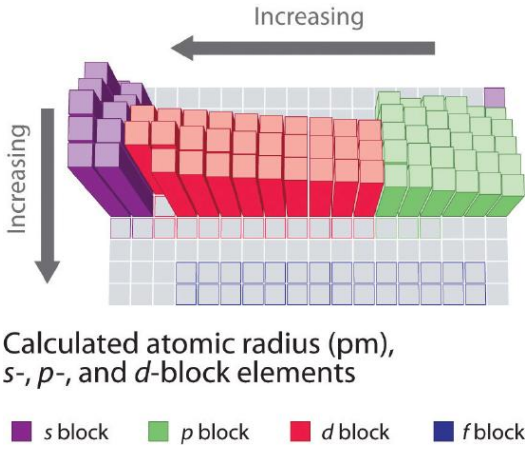



**Figure 3.2.5 The Atomic Radius of the Elements.** *The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the*

*nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe] 5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

### Note the Pattern

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

### Example 3.2.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

**Given:** three elements

**Asked for:** arrange in order of increasing atomic radius

**Strategy:**

**A** Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.

**B** List the elements in order of increasing atomic radius.

**Solution:**

**A** These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater. **B** Combining the two inequalities gives the overall order: C < Si < Al.

Exercise

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

**Answer:** O < S < P < K

## Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 3.2.6 , the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the $Na^+$ ion is essentially the same in NaCl and $Na_2S$, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

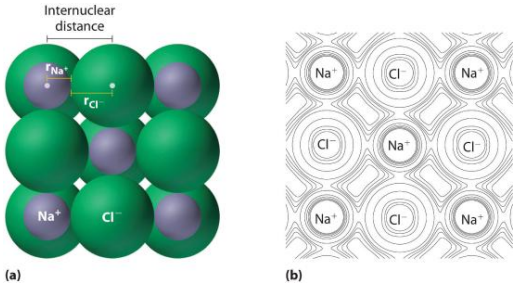
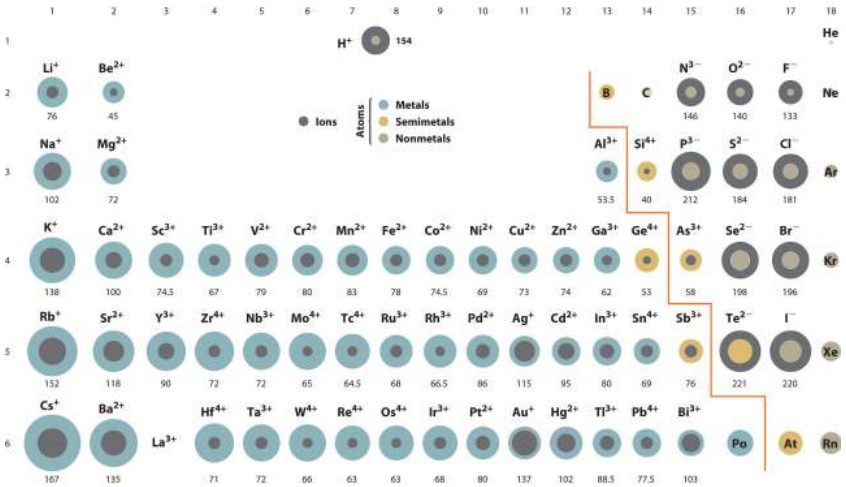



Figure 3.2.6 Definition of Ionic Radius. *(a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for $Na^+$ and $Cl^-$ in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around $Cl^-$ and $Na^+$.*

A comparison of ionic radii with atomic radii (Figure 3.2.7) *cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom.* When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases (compare Li at 167 pm with $Li^+$ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare $Fe^{2+}$ at 78 pm with $Fe^{3+}$ at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases (compare F at 42 pm with $F^-$ at 133 pm).




**3.2.7 Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements.** *Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms, previously shown in Figure 3.7 . Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.*

## Note the Pattern

Cations are always smaller than the neutral atom, and anions are always larger.

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the $Na^-$ ion, allowing comparison of its size with that of the far more familiar $Na^+$ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 3.2.1. All three species have a nuclear charge of +11, but they contain 10 ($Na^+$), 11 ($Na^0$), and 12 ($Na^-$) electrons. The $Na^+$ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The $Na^-$ ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

**Table 3.2.1 Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States**

| | $Na^+$ | $Na^0$ | $Na^-$ |
|---|---|---|---|
| Electron configuration | $1s^2 2s^2 2p^6$ | $1s^2 2s^2 2p^6 3s^1$ | $1s^2 2s^2 2p^6 3s^2$ |
| Radius (pm | 102 | 154* | 202* |

* The metallic radius measured for Na

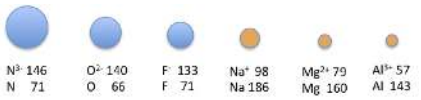
Source: M.J. Wagner and J.L. Dye "Alkalides, Electrides and Expanded Metals," *Annual Review of Materials Science* **23** (1993) 225-253.

## Contributors

- Anonymous

Modified by Joshua Halpern

. The sizes of the ions in this series decrease smoothly from $N^{3-}$ to $Al^{3+}$. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge ($Al^{3+}$) is the smallest, and the ion with the smallest nuclear charge ($N^{3-}$) is the largest. One member of this isoelectronic series is not listed in Table 3.2.3 : the neon atom. Because neon forms no covalent or ionic compounds, its radius is difficult to measure.




| Ion | Radius (pm) | Atomic Number |
|---|---|---|
| $N^{3-}$ | 146 | 7 |
| $O^{2-}$ | 140 | 8 |
| $F^{-}$ | 133 | 9 |
| $Na^{+}$ | 98 | 11 |
| $Mg^{2+}$ | 79 | 12 |
| $Al^{3+}$ | 57 | 13 |

**Table 3.2.3 Radius of Ions with the Neon Closed-Shell Electron Configuration.** Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

## Example 3.2.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: $Cl^{-}$, $K^{+}$, $S^{2-}$, and $Se^{2-}$.

**Given:** four ions

**Asked for:** order by increasing radius

**Strategy:**

**A** Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

**B** Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

**Solution:**

**A** We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. $K^{+}$, $Cl^{-}$, and $S^{2-}$ form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because $K^{+}$ has the greatest nuclear charge ($Z = 19$), its radius is smallest, and $S^{2-}$ with $Z = 16$ has the largest radius. Because selenium is directly below sulfur, we expect the $Se^{2-}$ ion to be even larger than $S^{2-}$. **B** The order must therefore be $K^{+} < Cl^{-} < S^{2-} < Se^{2-}$.

Exercise

Based on their positions in the periodic table, arrange these ions in order of increasing size: $Br^{-}$, $Ca^{2+}$, $Rb^{+}$, and $Sr^{2+}$.

**Answer:** $Ca^{2+} < Sr^{2+} < Rb^{+} < Br^{-}$

## Summary

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius ($r_{cov}$)** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius ($r_{met}$)** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius ($r_{vdW}$)** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

## Key Takeaway

- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

## Conceptual Problems

1. The electrons of the 1*s* shell have a stronger electrostatic attraction to the nucleus than electrons in the 2*s* shell. Give two reasons for this.
2. Predict whether Na or Cl has the more stable $1s^2$ shell and explain your rationale.
3. Arrange K, F, Ba, Pb, B, and I in order of decreasing atomic radius.
4. Arrange Ag, Pt, Mg, C, Cu, and Si in order of increasing atomic radius.
5. Using the periodic table, arrange Li, Ga, Ba, Cl, and Ni in order of increasing atomic radius.
6. Element M is a metal that forms compounds of the type $MX_2$, $MX_3$, and $MX_4$, where X is a halogen. What is the expected trend in the ionic radius of M in these compounds? Arrange these compounds in order of decreasing ionic radius of M.
7. The atomic radii of Na and Cl are 190 and 79 pm, respectively, but the distance between sodium and chlorine in NaCl is 282 pm. Explain this discrepancy.
8. Are shielding effects on the atomic radius more pronounced across a row or down a group? Why?
9. What two factors influence the size of an ion relative to the size of its parent atom? Would you expect the ionic radius of $S^{2-}$ to be the same in both MgS and $Na_2S$? Why or why not?
10. Arrange $Br^-$, $Al^{3+}$, $Sr^{2+}$, $F^-$, $O^{2-}$, and $I^-$ in order of increasing ionic radius.
11. Arrange $P^{3-}$, $N^{3-}$, $Cl^-$, $In^{3+}$, and $S^{2-}$ in order of decreasing ionic radius.
12. How is an isoelectronic series different from a series of ions with the same charge? Do the cations in magnesium, strontium, and potassium sulfate form an isoelectronic series? Why or why not?
13. What isoelectronic series arises from fluorine, nitrogen, magnesium, and carbon? Arrange the ions in this series by
    1. increasing nuclear charge.
    2. increasing size.
14. What would be the charge and electron configuration of an ion formed from calcium that is isoelectronic with
    1. a chloride ion?
    2. $Ar^+$?

## Answers

1. The 1*s* shell is closer to the nucleus and therefore experiences a greater electrostatic attraction. In addition, the electrons in the 2*s* subshell are shielded by the filled $1s^2$ shell, which further decreases the electrostatic attraction to the nucleus.
2. 
3. Ba > K > Pb > I > B > F
4. 
5. 
6. 
7. The sum of the calculated atomic radii of sodium and chlorine *atoms* is 253 pm. The sodium cation is significantly smaller than a neutral sodium atom (102 versus 154 pm), due to the loss of the single electron in the 3*s* orbital. Conversely, the chloride ion is much larger than a neutral chlorine atom (181 versus 99 pm), because the added electron results in greatly increased electron–electron repulsions within the filled $n = 3$ principal shell. Thus, transferring an electron from sodium to chlorine decreases the radius of sodium by about 50%, but causes the radius of chlorine to almost double. The net effect is that the distance between a sodium ion and a chloride ion in NaCl is *greater* than the sum of the atomic radii of the neutral atoms.
8. 
9. 
10. 
11. 
12. 
13. 
14. 

## Numerical Problems

1. Plot the ionic charge versus ionic radius using the following data for Mo: $Mo^{3+}$, 69 pm; $Mo^{4+}$, 65 pm; and $Mo^{5+}$, 61 pm. Then use this plot to predict the ionic radius of $Mo^{6+}$. Is the observed trend consistent with the general trends discussed in the chapter? Why or why not?

2. Internuclear distances for selected ionic compounds are given in the following table.
    1. If the ionic radius of $Li^+$ is 76 pm, what is the ionic radius of each of the anions?

| | LiF | LiCl | LiBr | LiI |
|---|---|---|---|---|
| Distance (pm) | 209 | 257 | 272 | 296 |

    2. What is the ionic radius of $Na^+$?

| | NaF | NaCl | NaBr | NaI |
|---|---|---|---|---|
| Distance (pm) | 235 | 282 | 298 | 322 |

3. Arrange the gaseous species $Mg^{2+}$, $P^{3-}$, $Br^-$, $S^{2-}$, $F^-$, and $N^{3-}$ in order of increasing radius and justify your decisions.

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# 7.3: The Chemical Families

**Learning Objectives**

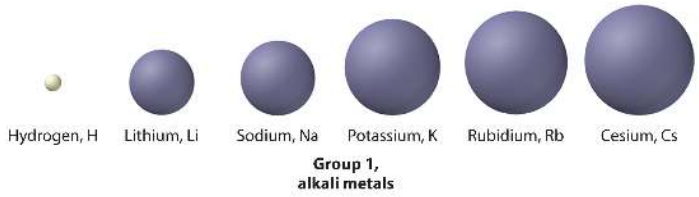
- To understand the correlation between the chemical properties and the reactivity of the elements and their positions in the periodic table

Periodic trends in properties such as atomic size and ionic size, ionization energy, electron affinity, and electronegativity illustrate the strong connection between the **chemical properties** and the reactivity of the elements and their positions in the periodic table. In this section, we explore that connection by focusing on two periodic properties that correlate strongly with the chemical behavior of the elements: valence electron configurations and Mulliken electronegativities.

## The Main Group Elements

We have said that elements with the same valence electron configuration (i.e., elements in the same column of the periodic table) often have similar chemistry. This correlation is particularly evident for the elements of groups 1, 2, 3, 13, 16, 17, and 18. The intervening families in the *p* block (groups 14 and 15) straddle the diagonal line separating metals from nonmetals. The lightest members of these two families are nonmetals, so they react differently compared to the heaviest members, which are metals. We begin our survey with the alkali metals (group 1), which contain only a single electron outside a noble gas electron configuration, and end with the noble gases (group 18), which have full valence electron shells.

## Group 1: The Alkali Metals




The elements of group 1 are called the *alkali metals*. *Alkali* (from the Arabic *al-qili*, meaning “ashes of the saltwort plant from salt marshes”) was a general term for substances derived from wood ashes, all of which possessed a bitter taste and were able to neutralize acids. Although oxides of both group 1 and group 2 elements were obtained from wood ashes, the alkali metals had lower melting points.

Potassium and sodium were first isolated in 1807 by the British chemist Sir Humphry Davy (1778–1829) by passing an electrical current through molten samples of potash ($K_2CO_3$) and soda ash ($Na_2CO_3$). The potassium burst into flames as soon as it was produced because it reacts readily with oxygen at the higher temperature. However, the group 1 elements, like the group 2 elements, become less reactive with air or water as their atomic number decreases. The heaviest element (francium) was not discovered until 1939. It is so radioactive that studying its chemistry is very difficult.

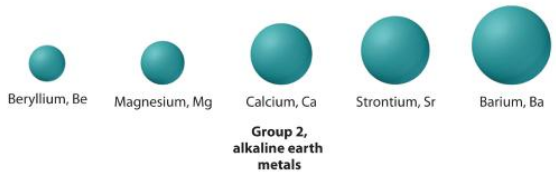
The alkali metals have $ns^1$ valence electron configurations and the lowest electronegativity of any group; hence they are often referred to as being *electropositive* elements. As a result, they have a strong tendency to lose their single valence electron to form compounds in the +1 oxidation state, producing the EX monohalides and the $E_2O$ oxides.

Reducing agents are species that can lose an electron in a reaction. Alkalai metals with only a single s electron, and very low ionization energies can easily do this and thus are powerful reducing agents. Sodium salts such as common table salt (NaCl), baking soda ($NaHCO_3$), soda ash ($Na_2CO_3$), and caustic soda (NaOH) are important industrial chemicals. Other compounds of the alkali metals are important in biology. For example, because potassium is required for plant growth, its compounds are used in fertilizers, and lithium salts are used to treat manic-depressive, or bipolar, disorders. The best modern batteries use lithium.

We can watch a video demonstration of the properties of lithium, sodium and potassium. Rubidium and cesium are extremely reactive and difficult to handle in the atmosphere when there is any water vapor present




## Group 2: The Alkaline Earth Metals

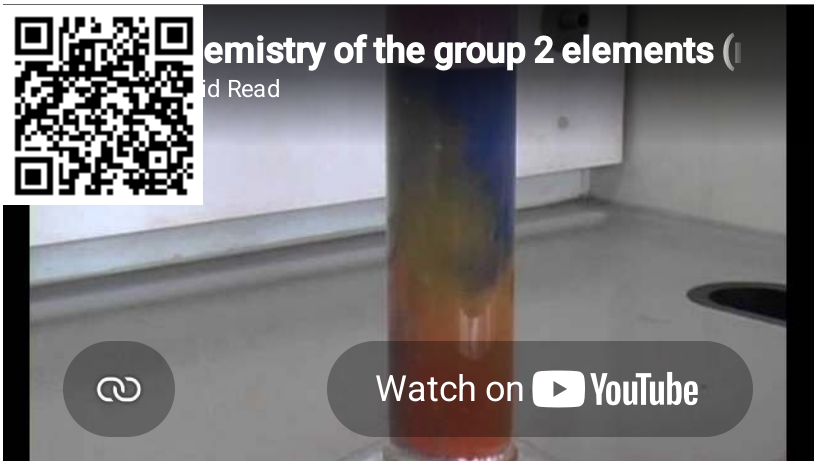



The elements of group 2 are collectively referred to as the *alkaline earth metals*, a name that originated in the Middle Ages, when an "earth" was defined as a substance that did not melt and was not transformed by fire. Alkalis that did not melt easily were called "alkaline earths."

Recall that the trend in most groups is for the lightest member to have properties that are quite different from those of the heavier members. Consistent with this trend, the properties of the lightest element—in this case, beryllium—tend to be different from those of its heavier *congeners*, the other members of the group. Beryllium is relatively unreactive but forms many covalent compounds, whereas the other group members are much more reactive metals and form ionic compounds. As is the case with the alkali metals, the heaviest element, radium, is highly radioactive, making its size difficult to measure. Radium was discovered in 1902 by Marie Curie (1867–1934; Nobel Prize in Chemistry 1903 and Nobel Prize in Chemistry 1911), who, with her husband, Pierre, isolated 120 mg of radium chloride from tons of residues from uranium mining.

All the alkaline earth metals have $ns^2$ valence electron configurations, and all have electronegativities less than 1.6. This means that they behave chemically as metals (although beryllium compounds are covalent) and lose the two valence electrons to form compounds in the +2 oxidation state. Examples include the dihalides ($EX_2$) and the oxides (EO).

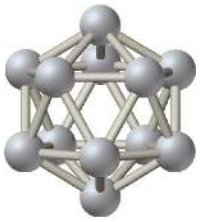
Compounds of the group 2 elements have been commercially important since Egyptian and Roman times, when blocks of limestone or marble, which are both $CaCO_3$, were used as building materials, and gypsum ($CaSO_4 \cdot 2\ H_2O$) or lime (CaO) was used as mortar. Calcium sulfate is still used in Portland cement and plaster of Paris. Magnesium and beryllium form lightweight, high-strength alloys that are used in the aerospace, automotive, and other high-tech industries. As you learned previously, one of the most impressive uses of these elements is in fireworks; strontium and barium salts, for example, give red or green colors, respectively. Except for beryllium, which is highly toxic when powdered, the group 2 elements are also important biologically. Bone is largely hydroxyapatite [$Ca_5(PO_4)_3OH$], mollusk shells are calcium carbonate, magnesium is part of the chlorophyll molecule in green plants, and calcium is important in hormonal and nerve signal transmission. Because $BaSO_4$ is so insoluble, it is used in "barium milk shakes" to obtain x-rays of the gastrointestinal tract. Reaction of the Alkaline earth metals with water is not quite so. . . .exciting as that of the alkalai metals as seen in this video from the University of Southampton




## Group 13




Of the group 13 elements, only the lightest, boron, lies on the diagonal line that separates nonmetals and metals. Thus boron is a semimetal, whereas the rest of the group 13 elements are metals. Elemental boron has an unusual structure consisting of $B_{12}$ icosahedra covalently bonded to one another; the other elements are typical metallic solids.



$B_{12}$ icosahedron in elemental boron

No group 13 elements were known in ancient times, not because they are scarce—Al is the third most abundant element in Earth's crust—but because they are highly reactive and form extremely stable compounds with oxygen. To isolate the pure elements, potent reducing agents and careful handling were needed.

The elements of group 13 have $ns^2np^1$ valence electron configurations. Consequently, two oxidation states are important: +3, from losing three valence electrons to give the closed-shell electron configuration of the preceding noble gas; and +1, from losing the single electron in the *np* subshell. Because these elements have small, negative electron affinities (boron's is only −27.0 kJ/mol), they are unlikely to acquire five electrons to reach the next noble gas configuration. In fact, the chemistry of these elements is almost exclusively characterized by +3. Only the heaviest element (Tl) has extensive chemistry in the +1 oxidation state. It loses the single 6*p* electron to produce TlX monohalides and the oxide $Tl_2O$.

In the 19th century, aluminum was considered a precious metal. In fact, it was considered so precious that aluminum knives and forks were reserved for the French Emperor Louis Napoleon III, while his less important guests had to be content with gold or silver cutlery. Because of the metal's rarity the dedication of the Washington Monument in 1885 was celebrated by placing a 100 oz chunk of pure aluminum at the top. In contrast, today aluminum is used on an enormous scale in aircraft, automobile engines, armor, cookware, and beverage containers. It is valued for its combination of low density, high strength, and corrosion resistance. Aluminum is also found in compounds that are the active ingredients in most antiperspirant deodorants.

Compounds of boron, such as one form of BN, are hard, have a high melting point, and are resistant to corrosion. They are particularly useful in materials that are exposed to extreme conditions, such as aircraft turbines, brake linings, and polishing

compounds. Boron is also a major component of many kinds of glasses, and sodium perborate [$Na_2B_2O_4(OH)_4$] is the active ingredient in many so-called color-safe laundry bleaches.

Gallium, indium, and thallium are less widely used, but gallium arsenide is the red light-emitting diode (LED) in digital readouts in electronics, and $MgGa_2O_4$ produces the green light emitted in many xerographic machines. Compounds of thallium(I) are extremely toxic. Although $Tl_2SO_4$ is an excellent rat or ant poison, it is so toxic to humans that it is no longer used for this purpose.

## Group 14




**Group 14**

The group 14 elements straddle the diagonal line that divides nonmetals from metals. Of the elements in this group, carbon is a nonmetal, silicon and germanium are semimetals, and tin and lead are metals. As a result of this diversity, the structures of the pure elements vary greatly.

The $ns^2np^2$ valence electron configurations of group 14 gives rise to three oxidation states: −4, in which four electrons are added to achieve the closed-shell electron configuration of the next noble gas; +4, in which all four valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and +2, in which the loss of two $np^2$ electrons gives a filled $ns^2$ subshell.

The electronegativity of carbon is only 2.5, placing it in the middle of the electronegativity range, so carbon forms covalent compounds with a wide variety of elements and is the basis of all organic compounds. All of the group 14 elements form compounds in the +4 oxidation state, so all of them are able to form dioxides (from $CO_2$ to $PbO_2$) and tetrachlorides ($CCl_4$ and $PbCl_4$). Only the two metallic elements, Sn and Pb, form an extensive series of compounds in the +2 oxidation state. Tin salts are sprayed onto glass to make an electrically conductive coating, and then the glass is used in the manufacture of frost-free windshields. Lead sulfate is formed when your car battery discharges.

Carbon has at least four allotropes (forms or crystal structures) that are stable at room temperature: graphite; diamond; a group of related cage structures called fullerenesOne of at least four allotropes of carbon comprising a group of related cage structures. (such as $C_{60}$); nanotubesOne of at least four allotropes of carbon that are cylinders of carbon atoms and are intermediate in structure between graphite and the fullerenes., which are cylinders of carbon atoms (Figure 3.4.1 ), and graphene which is a single atomic layer of carbon atoms covalently bonded. Graphite consists of extended planes of covalently bonded hexagonal rings. Because the planes are not linked by covalent bonds, they can slide across one another easily. This makes graphite ideally suited as a lubricant and as the “lead” in lead pencils mixed with a bit of clay as a binder. Graphite also provides the black color in inks and tires, and graphite fibers are used in high-tech items such as golf clubs, tennis rackets, airplanes, and sailboats because of their lightweight, strength, and stiffness.

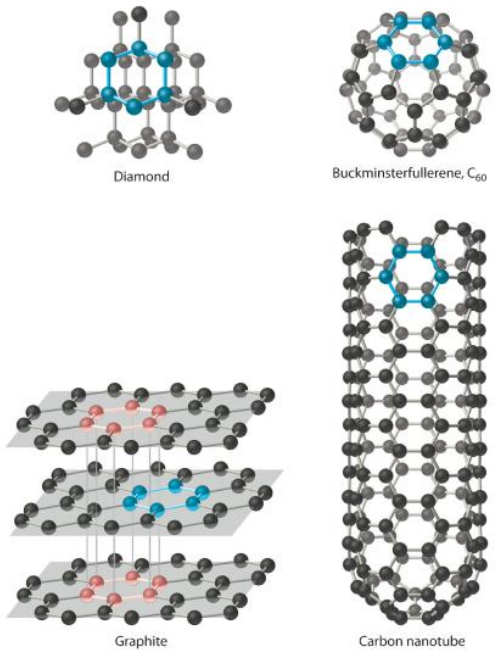



Figure 3.4.1 Four Allotropes of **Carbon.** *Diamond consists of a rigid three-dimensional array of carbon atoms, making it one of the hardest substances known. In contrast, graphite forms from extended planes of covalently bonded hexagonal rings of carbon atoms that can slide across one another easily. Fullerenes are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms, and nanotubes are sheets of graphite rolled up into a cylinder.*

In contrast to the layered structure of graphite, each carbon atom in diamond is bonded to four others to form a rigid three-dimensional array, making diamond one of the hardest substances known; consequently, it is used in industry as a cutting tool. Fullerenes, on the other hand, are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms; they are volatile substances that dissolve in organic solvents. Fullerenes of extraterrestrial origin have been found in meteorites and have been discovered in a cloud of cosmic dust surrounding a distant star, which makes them the largest molecules ever seen in space. Carbon nanotubes, intermediate in structure between graphite and the fullerenes, can be described as sheets of graphite that have been rolled up into a cylinder or, alternatively, fullerene cages that have been stretched in one direction. Carbon nanotubes are being studied for use in the construction of molecular electronic devices and computers. For example, fabrics that are dipped in an ink of nanotubes and then pressed to thin out the coating are turned into batteries that maintain their flexibility. This creates "wearable electronics" and allows for the possibility of incorporating electronics into flexible surfaces. When applied to a t-shirt, for example, the t-shirt is converted into an "e-shirt."

Silicon is the second must abundant element in Earth's crust. Both silicon and germanium have strong, three-dimensional network structures similar to that of diamond. Sand is primarily $SiO_2$, which is used commercially to make glass and prevent caking in food products. Complex compounds of silicon and oxygen with elements such as aluminum are used in detergents and talcum powder and as industrial catalysts. Because silicon-chip technology laid the foundation for the modern electronics industry, the San Jose region of California, where many of the most important advances in electronics and computers were developed, has been nicknamed "Silicon Valley."

Elemental tin and lead are metallic solids. Tin is primarily used to make alloys such as bronze, which consists of tin and copper; solder, which is tin and lead; and pewter, which is tin, antimony, and copper.

In ancient times, lead was used for everything from pipes to cooking pots because it is easily hammered into different shapes. In fact, the term *plumbing* is derived from *plumbum*, the Latin name for lead. Lead compounds were used as pigments in paints, and tetraethyllead was an important antiknock agent in gasoline. Now, however, lead has been banned from many uses because of its toxicity, although it is still widely used in lead storage batteries for automobiles. In previous centuries, lead salts were frequently used as medicines. Evidence suggests, for example, that Beethoven's death was caused by the application of various lead-containing medicines by his physician. Beethoven contracted pneumonia and was treated with lead salts, but in addition, he

suffered from a serious liver ailment. His physician treated the ailment by repeatedly puncturing his abdominal cavity and then sealing the wound with a lead-laced poultice. It seems that the repeated doses of lead compounds contributed to Beethoven's death.

## Group 15: The Pnicogens




The group 15 elements are called the pnicogensThe elements in group 15 of the periodic table.—from the Greek *pnigein*, meaning "to choke," and *genes*, meaning "producing"—ostensibly because of the noxious fumes that many nitrogen and phosphorus compounds produce. This family has five stable elements; one isotope of bismuth ($^{209}Bi$) is nonradioactive and is the heaviest nonradioactive isotope of any element. Once again, the lightest member of the family has unique properties. Although both nitrogen and phosphorus are nonmetals, nitrogen under standard conditions is a diatomic gas ($N_2$), whereas phosphorus consists of three allotropes: white, a volatile, low-melting solid consisting of $P_4$ tetrahedra; a red solid comprised of $P_8$, $P_9$, and $P_{10}$ cages linked by $P_2$ units; and black layers of corrugated phosphorus sheets. The next two elements, arsenic and antimony, are semimetals with extended three-dimensional network structures, and bismuth is a silvery metal with a pink tint.

All of the pnicogens have $ns^2np^3$ valence electron configurations, leading to three common oxidation states: −3, in which three electrons are added to give the closed-shell electron configuration of the next noble gas; +5, in which all five valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and +3, in which only the three *np* electrons are lost to give a filled $ns^2$ subshell. Because the electronegativity of nitrogen is similar to that of chlorine, nitrogen accepts electrons from most elements to form compounds in the −3 oxidation state (such as in $NH_3$). Nitrogen has only positive oxidation states when combined with highly electronegative elements, such as oxygen and the halogens (e.g., $HNO_3$, $NF_3$). Although phosphorus and arsenic can combine with active metals and hydrogen to produce compounds in which they have a −3 oxidation state ($PH_3$, for example), they typically attain oxidation states of +3 and +5 when combined with more electronegative elements, such as $PCl_3$ and $H_3PO_4$. Antimony and bismuth are relatively unreactive metals, but form compounds with oxygen and the halogens in which their oxidation states are +3 and +5 (as in $Bi_2O_3$ and $SbF_5$).

Although it is present in most biological molecules, nitrogen was the last pnicogen to be discovered. Nitrogen compounds such as ammonia, nitric acid, and their salts are used agriculturally in huge quantities; nitrates and nitrites are used as preservatives in meat products such as ham and bacon, and nitrogen is a component of nearly all explosives.

Phosphorus, too, is essential for life, and phosphate salts are used in fertilizers, toothpaste, and baking powder. One, phosphorus sulfide, $P_4S_3$, is used to ignite modern safety matches. Arsenic, in contrast, is toxic; its compounds are used as pesticides and poisons. Antimony and bismuth are primarily used in metal alloys, but a bismuth compound is the active ingredient in the popular antacid medication Pepto-Bismol.

## Group 16: The Chalcogens




The group 16 elements are often referred to as the chalcogensThe elements in group 16 of the periodic table.—from the Greek *chalk*, meaning "copper," and *genes*, meaning "producing"—because the most ancient copper ore, copper sulfide, is also rich in two other group 16 elements: selenium and tellurium. Once again, the lightest member of the family has unique properties. In its most common pure form, oxygen is a diatomic gas ($O_2$), whereas sulfur is a volatile solid with $S_8$ rings, selenium and tellurium are gray or silver solids that have chains of atoms, and polonium is a silvery metal with a regular array of atoms. Like astatine and radon, polonium is a highly radioactive metallic element.

All of the chalcogens have $ns^2np^4$ valence electron configurations. Their chemistry is dominated by three oxidation states: −2, in which two electrons are added to achieve the closed-shell electron configuration of the *next* noble gas; +6, in which all six valence

electrons are lost to give the closed-shell electron configuration of the *preceding* noble gas; and +4, in which only the four *np* electrons are lost to give a filled $ns^2$ subshell. Oxygen has the second highest electronegativity of any element; its chemistry is dominated by the −2 oxidation state (as in MgO and $H_2O$). No compounds of oxygen in the +4 or +6 oxidation state are known. In contrast, sulfur can form compounds in all three oxidation states. Sulfur accepts electrons from less electronegative elements to give $H_2S$ and $Na_2S$, for example, and it donates electrons to more electronegative elements to give compounds such as $SO_2$, $SO_3$, and $SF_6$. Selenium and tellurium, near the diagonal line in the periodic table, behave similarly to sulfur but are somewhat more likely to be found in positive oxidation states.

Oxygen, the second most electronegative element in the periodic table, was not discovered until the late 18th century, even though it constitutes 20% of the atmosphere and is the most abundant element in Earth's crust. Oxygen is essential for life; our metabolism is based on the oxidation of organic compounds by $O_2$ to produce $CO_2$ and $H_2O$. Commercially, oxygen is used in the conversion of pig iron to steel, as the oxidant in oxyacetylene torches for cutting steel, as a fuel for the US space shuttle, and in hospital respirators.

Sulfur is the brimstone in "fire and brimstone" from ancient times. Partly as a result of its long history, it is employed in a wide variety of commercial products and processes. In fact, more sulfuric acid is produced worldwide than any other compound. Sulfur is used to cross-link the polymers in rubber in a process called *vulcanization*, which was discovered by Charles Goodyear in the 1830s and commercialized by Benjamin Goodrich in the 1870s. Vulcanization gives rubber its unique combination of strength, elasticity, and stability.

Selenium, the only other commercially important chalcogen, was discovered in 1817, and today it is widely used in light-sensitive applications. For example, photocopying, or xerography, from the Greek *xèrós*, meaning "dry," and *graphia*, meaning "writing," uses selenium films to transfer an image from one piece of paper to another, while compounds such as cadmium selenide are used to measure light in photographic light meters and automatic streetlights.

## Group 17: The Halogens




The term *halogen*, derived from the Greek *háls*, meaning "salt," and *genes*, meaning "producing," was first applied to chlorine because of its tendency to react with metals to form salts. All of the halogens have an $ns^2np^5$ valence electron configuration, and all but astatine are diatomic molecules in which the two halogen atoms share a pair of electrons. Diatomic $F_2$ and $Cl_2$ are pale yellow-green and pale green gases, respectively, while $Br_2$ is a red liquid, and $I_2$ is a purple solid. The halogens were not isolated until the 18th and 19th centuries.

Because of their relatively high electronegativities, the halogens are nonmetallic and generally react by gaining one electron per atom to attain a noble gas electron configuration and an oxidation state of −1. *Halides* are produced according to the following equation, in which X denotes a halogen:

$$2E + nX_2 \rightarrow 2EX_n$$

If the element E has a low electronegativity (as does Na), the product is typically an ionic halide (NaCl). If the element E is highly electronegative (as P is), the product is typically a covalent halide ($PCl_5$). Ionic halides tend to be nonvolatile substances with high melting points, whereas covalent halides tend to be volatile substances with low melting points. Fluorine is the most reactive of the halogens, and iodine the least, which is consistent with their relative electronegativities (Figure 3.3.11 ).As we shall see in subsequent chapters, however, factors such as bond strengths are also important in dictating the reactivities of these elements. In fact, fluorine reacts with nearly all elements at room temperature. Under more extreme conditions, it combines with all elements except helium, neon, and argon.

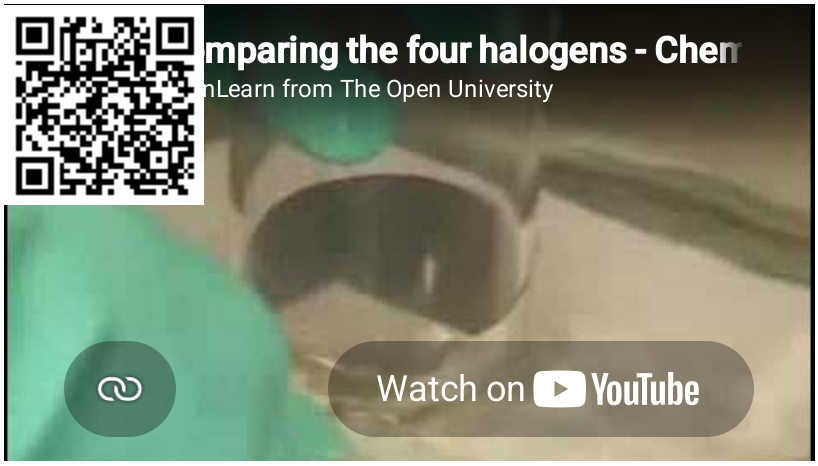
The halogens react with hydrogen to form the hydrogen halides (HX):

$$H_2(g) + X_2(g,l,s) \rightarrow 2\,HX(g) \quad H_2\,(g) + X_2\,(g,l,s) \rightarrow 2HX(g) \quad (3.4.2)$$

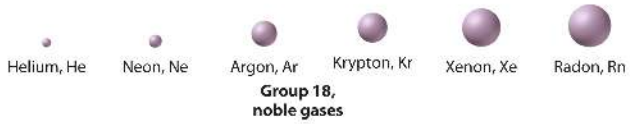
Fluorine is so reactive that any substance containing hydrogen, including coal, wood, and even water, will burst into flames if it comes into contact with pure $F_2$.

Because it is the most electronegative element known, fluorine never has a positive oxidation state in any compound. In contrast, the other halogens (Cl, Br, I) form compounds in which their oxidation states are +1, +3, +5, and +7, as in the *oxoanions*, $XO_n^-$, where $n$ = 1–4. Because oxygen has the second highest electronegativity of any element, it stabilizes the positive oxidation states of the halogens in these ions.

All of the halogens except astatine (which is radioactive) are commercially important. NaCl in salt water is purified for use as table salt. Chlorine and hypochlorite ($OCl^-$) salts are used to sanitize public water supplies, swimming pools, and wastewater, and hypochlorite salts are also used as bleaches because they oxidize colored organic molecules. Organochlorine compounds are used as drugs and pesticides. Fluoride (usually in the form of NaF) is added to many municipal water supplies to help prevent tooth decay, and bromine (in AgBr) is a component of the light-sensitive coating on photographic film. Because iodine is essential to life—it is a key component of the hormone produced by the thyroid gland—small amounts of KI are added to table salt to produce "iodized salt," which prevents thyroid hormone deficiencies. The video shows the (some times explosive) reactions of the halogens



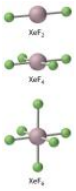

## Group 18: The Noble Gases




The noble gases are helium, neon, argon, krypton, xenon, and radon. All have filled valence electron configurations and therefore are unreactive elements found in nature as monatomic gases. The noble gases were long referred to as either "rare gases" or "inert gases," but they are neither rare nor inert. Argon constitutes about 1% of the atmosphere, which also contains small amounts of the lighter group 18 elements, and helium is found in large amounts in many natural gas deposits. The group's perceived "rarity" stems in part from the fact that the noble gases were the last major family of elements to be discovered.

The noble gases have $EA \geq 0$, so they do not form compounds in which they have negative oxidation states. Because ionization energies decrease down the column, the only noble gases that form compounds in which they have positive oxidation states are Kr, Xe, and Rn. Of these three elements, only xenon forms an extensive series of compounds. The chemistry of radon is severely limited by its extreme radioactivity, and the chemistry of krypton is limited by its high ionization energy (1350.8 kJ/mol versus 1170.4 kJ/mol for xenon). In essentially all its compounds, xenon is bonded to highly electronegative atoms such as fluorine or oxygen. In fact, the only significant reaction of xenon is with elemental fluorine, which can give $XeF_2$, $XeF_4$, or $XeF_6$. Oxides such as $XeO_3$ are produced when xenon fluorides react with water, and oxidation with ozone produces the perxenate ion [$XeO_6^{4-}$], in which xenon acquires a +8 oxidation state by formally donating all eight of its valence electrons to the more electronegative oxygen atoms. In all of its stable compounds, xenon has a positive, even-numbered oxidation state: +2, +4, +6, or +8. The actual stability of these compounds varies greatly. For example, $XeO_3$ is a shock-sensitive, white crystalline solid with explosive power comparable to that of TNT (trinitrotoluene), whereas another compound, $Na_2XeF_8$, is stable up to 300°C.

Although none of the noble gas compounds is commercially significant, the elements themselves have important applications. For example, argon is used in incandescent light bulbs, where it provides an inert atmosphere that protects the tungsten filament from oxidation, and in compact fluorescent light bulbs (CFLs). It is also used in arc welding and in the manufacture of reactive elements, such as titanium, or of ultrapure products, such as the silicon used by the electronics industry. Helium, with a boiling point of only 4.2 K, is used as a liquid for studying the properties of substances at very low temperatures. It is also combined in an 80:20 mixture with oxygen used by scuba divers, rather than compressed air, when they descend to great depths. Because helium is less soluble in water than $N_2$—a component of compressed air—replacing $N_2$ with He prevents the formation of bubbles in blood vessels, a condition called “the bends” that can occur during rapid ascents. Neon is familiar to all of us as the gas responsible for the red glow in neon lights.



## The Transition Metals, the Lanthanides, and the Actinides

As expected for elements with the same valence electron configuration, the elements in each column of the *d* block have vertical similarities in chemical behavior. In contrast to the *s*- and *p*-block elements, however, elements in the *d* block also display strong *horizontal* similarities. The horizontal trends compete with the vertical trends. In further contrast to the *p*-block elements, which tend to have stable oxidation states that are separated by *two* electrons, the transition metalsAny element in groups 3–12 in the periodic table. All of the transition elements are metals. have multiple oxidation states that are separated by only *one* electron.

### Note the Pattern

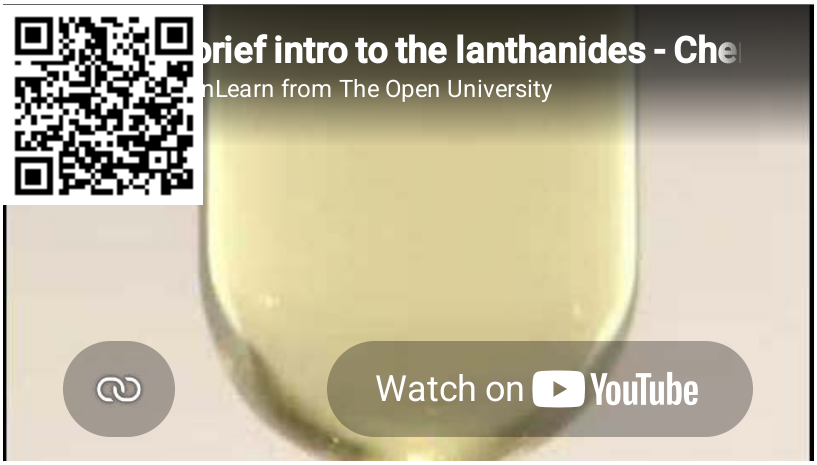
The *p*-block elements form stable compounds in oxidation states that tend to be separated by two electrons, whereas the transition metals have multiple oxidation states that are separated by one electron.

The group 6 elements, chromium, molybdenum, and tungsten, illustrate the competition that occurs between these horizontal and vertical trends. For example, the maximum number of electrons that can be lost for all elements in group 6 is +6, achieved by losing all six valence electrons (recall that Cr has a $4s^1 3d^5$ valence electron configuration), yet nearly all the elements in the first row of the transition metals, including chromium, form compounds with the dication $M^{2+}$, and many also form the trication $M^{3+}$. As a result, the transition metals in group 6 have very different tendencies to achieve their maximum oxidation state. The most common oxidation state for chromium is +3, whereas the most common oxidation state for molybdenum and tungsten is +6.

### Note the Pattern

The *d*-block elements display both strong vertical and horizontal similarities.

Groups 3 (scandium, lanthanum, actinium), 11 (copper, silver, gold), and 12 (zinc, cadmium, mercury) are the only transition metal groups in which the oxidation state predicted by the valence electron configuration dominates the chemistry of the group. The elements of group 3 have three valence electrons outside an inner closed shell, so their chemistry is almost exclusively that of the $M^{3+}$ ions produced by losing all three valence electrons. The elements of group 11 have 11 valence electrons in an $ns^1(n-1)d^{10}$ valence electron configuration, and so all three lose a single electron to form the monocation $M^+$ with a closed $(n-1)d^{10}$ electron configuration. Consequently, compounds of $Cu^+$, $Ag^+$, and $Au^+$ are very common, although there is also a great deal of chemistry involving $Cu^{2+}$. Similarly, the elements of group 12 all have an $ns^2(n-1)d^{10}$ valence electron configuration, so they lose two electrons to form $M^{2+}$ ions with an $(n-1)d^{10}$ electron configuration; indeed, the most important ions for these elements are $Zn^{2+}$, $Cd^{2+}$, and $Hg^{2+}$. Mercury, however, also forms the dimeric mercurous ion ($Hg_2^{2+}$) because of a subtle balance between the energies needed to remove additional electrons and the energy released when bonds are formed. The +3 oxidation state is the most important for the lanthanidesAny of the 14 elements between Z=58 (cerium) and Z=71 (lutetium) and for most of the actinides (Any of the 14 elements between Z=90 (thorium) and Z=103 (lawrencium).) Why? Here is a brief video on the properties of the Lanthanides




## Example 8

Based on the following information, determine the most likely identities for elements D and E.

1. Element D is a shiny gray solid that conducts electricity only moderately; it forms two oxides ($DO_2$ and $DO_3$).
2. Element E is a reddish metallic substance that is an excellent conductor of electricity; it forms two oxides (EO and $E_2O$) and two chlorides (ECl and $ECl_2$).

**Given:** physical and chemical properties of two elements

**Asked for:** identities

**Strategy:**

**A** Based on the conductivity of the elements, determine whether each is a metal, a nonmetal, or a semimetal. Confirm your prediction from its physical appearance.

**B** From the compounds each element forms, determine its common oxidation states.

**C** If the element is a nonmetal, it must be located in the *p* block of the periodic table. If a semimetal, it must lie along the diagonal line of semimetals from B to At. Transition metals can have two oxidation states separated by one electron.

**D** From your classification, the oxidation states of the element, and its physical appearance, deduce its identity.

**Solution:**

1. **A** The moderate electrical conductivity of element D tells us that it is a semimetal. It must lie in the *p* block of the periodic table because all of the semimetals are located there. **B** The stoichiometry of the oxides tells us that two common oxidation states for D are +4 and +6. **C** Element D must be located in group 16 because the common oxidation states for the chalcogens (group 16) include +6 (by losing all six valence elections) and +4 (by losing the four electrons from the *p* subshell). Thus D is likely to be Se or Te. **D** Additional information is needed to distinguish between the two.
2. **A** Element E is an excellent electrical conductor, so it is a metal. **B** The stoichiometry of the oxides and chlorides, however, tells us that common oxidation states for E are +2 and +1. **C** Metals that can have two oxidation states separated by one electron are usually transition metals. The +1 oxidation state is characteristic of only one group: group 11. Within group 11, copper is the only element with common oxidation states of +1 and +2. **D** Copper also has a reddish hue. Thus element E is probably copper.

Exercise

Based on the following information, determine the most likely identities for elements G and J.

1. Element G is a red liquid that does not conduct electricity. It forms three compounds with fluorine (GF, $GF_3$, and $GF_5$) and one with sodium (NaG).
2. Element J is a soft, dull gray solid that conducts electricity well and forms two oxides (JO and $JO_2$).

**Answer**

1. Br

2. Sn or Pb

## Summary

The chemical families consist of elements that have the same valence electron configuration and tend to have similar chemistry. The alkali metals (group 1) have $ns^1$ valence electron configurations and form $M^+$ ions, while the alkaline earth metals (group 2) have $ns^2$ valence electron configurations and form $M^{2+}$ ions. Group 13 elements have $ns^2np^1$ valence electron configurations and have an overwhelming tendency to form compounds in the +3 oxidation state. Elements in group 14 have $ns^2np^2$ valence electron configurations but exhibit a variety of chemical behaviors because they range from a nonmetal (carbon) to metals (tin/lead). Carbon, the basis of organic compounds, has at least four allotropes with distinct structures: diamond, graphite, **fullerenes**, and carbon **nanotubes**. The **pnicogens** (group 15) all have $ns^2np^3$ valence electron configurations; they form compounds in oxidation states ranging from −3 to +5. The **chalcogens** (group 16) have $ns^2np^4$ valence electron configurations and react chemically by either gaining two electrons or by formally losing four or six electrons. The halogens (group 17) all have $ns^2np^5$ valence electron configurations and are diatomic molecules that tend to react chemically by accepting a single electron. The noble gases (group 18) are monatomic gases that are chemically quite unreactive due to the presence of a filled shell of electrons. The **transition metals** (groups 3–10) contain partially filled sets of *d* orbitals, and the **lanthanides** and the **actinides** are those groups in which *f* orbitals are being filled. These groups exhibit strong horizontal similarities in behavior. Many of the transition metals form $M^{2+}$ ions, whereas the chemistry of the lanthanides and actinides is dominated by $M^{3+}$ ions.

## Key Takeaway

- Periodic properties and the chemical behavior of the elements correlate strongly with valence electron configurations and Mulliken electronegativities.

## Conceptual Problems

1. Of the group 1 elements, which would you expect to be the best reductant? Why? Would you expect boron to be a good reductant? Why or why not?
2. Classify each element as a metal, a nonmetal, or a semimetal: Hf, I, Tl, S, Si, He, Ti, Li, and Sb. Which would you expect to be good electrical conductors? Why?
3. Classify each element as a metal, a nonmetal, or a semimetal: Au, Bi, P, Kr, V, Na, and Po. Which would you expect to be good electrical insulators? Why?
4. Of the elements Kr, Xe, and Ar, why does only xenon form an extensive series of compounds? Would you expect $Xe^{2+}$ to be a good oxidant? Why or why not?
5. Identify each statement about the halogens as either true or false and explain your reasoning.
    1. Halogens have filled valence electron configurations.
    2. Halogens tend to form salts with metals.
    3. As the free elements, halogens are monatomic.
    4. Halogens have appreciable nonmetallic character.
    5. Halogens tend to have an oxidation state of −1.
    6. Halogens are good reductants.
6. Nitrogen forms compounds in the +5, +4, +3, +2, and −3 oxidation states, whereas Bi forms ions only in the +5 and +3 oxidation states. Propose an explanation for the differences in behavior.
7. Of the elements Mg, Al, O, P, and Ne, which would you expect to form covalent halides? Why? How do the melting points of covalent halides compare with those of ionic halides?
8. Of the elements Li, Ga, As, and Xe, would you expect to form ionic chlorides? Explain your reasoning. Which are usually more volatile—ionic or covalent halides? Why?
9. Predict the relationship between the oxidative strength of the oxoanions of bromine—$BrO_n^-$ ($n$ = 1–4)—and the number of oxygen atoms present ($n$). Explain your reasoning.
10. The stability of the binary hydrides of the chalcogens decreases in the order $H_2O > H_2S > H_2Se > H_2Te$. Why?

11. Of the elements O, Al, H, and Cl, which will form a compound with nitrogen in a positive oxidation state? Write a reasonable chemical formula for an example of a binary compound with each element.
12. How do you explain the differences in chemistry observed for the group 14 elements as you go down the column? Classify each group 14 element as a metal, a nonmetal, or a semimetal. Do you expect the group 14 elements to form covalent or ionic compounds? Explain your reasoning.
13. Why is the chemistry of the group 13 elements less varied than the chemistry of the group 15 elements? Would you expect the chemistry of the group 13 elements to be more or less varied than that of the group 17 elements? Explain your reasoning.
14. If you needed to design a substitute for $BaSO_4$, the barium milkshake used to examine the large and small intestine by x-rays, would $BeSO_4$ be an inappropriate substitute? Explain your reasoning.
15. The alkali metals have an $ns^1$ valence electron configuration, and consequently they tend to lose an electron to form ions with +1 charge. Based on their valence electron configuration, what other kind of ion can the alkali metals form? Explain your answer.
16. Would Mo or W be the more appropriate biological substitute for Cr? Explain your reasoning.

## Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. Nitrogen will have a positive oxidation state in its compounds with O and Cl, because both O and Cl are more electronegative than N. Reasonable formulas for binary compounds are: $N_2O_5$ or $N_2O_3$ and $NCl_3$.
12.
13.
14.
15.
16.

## Numerical Problems

1. Write a balanced equation for formation of $XeO_3$ from elemental Xe and $O_2$. What is the oxidation state of Xe in $XeO_3$? Would you expect Ar to undergo an analogous reaction? Why or why not?
2. Which of the *p*-block elements exhibit the greatest variation in oxidation states? Why? Based on their valence electron configurations, identify these oxidation states.
3. Based on its valence electron configuration, what are the three common oxidation states of selenium? In a binary compound, what atoms bonded to Se will stabilize the highest oxidation state? the lowest oxidation state?
4. Would you expect sulfur to be readily oxidized by HCl? Why or why not? Would you expect phosphorus to be readily oxidized by sulfur? Why or why not?
5. What are the most common oxidation states for the pnicogens? What factors determine the relative stabilities of these oxidation states for the lighter and the heavier pnicogens? What is likely to be the most common oxidation state for phosphorus and arsenic? Why?

6. Of the compounds $NF_3$, $NCl_3$, and $NI_3$, which would be the least stable? Explain your answer. Of the ions $BrO^-$, $ClO^-$, or $FO^-$, which would be the least stable? Explain your answer.
7. In an attempt to explore the chemistry of the superheavy element ununquadium, $Z = 114$, you isolated two distinct salts by exhaustively oxidizing metal samples with chlorine gas. These salts are found to have the formulas $MCl_2$ and $MCl_4$. What would be the name of ununquadium using Mendeleev's *eka*-notation?
8. Would you expect the compound $CCl_2$ to be stable? $SnCl_2$? Why or why not?
9. A newly discovered element (Z) is a good conductor of electricity and reacts only slowly with oxygen. Reaction of 1 g of Z with oxygen under three different sets of conditions gives products with masses of 1.333 g, 1.668 g, and 1.501 g, respectively. To what family of elements does Z belong? What is the atomic mass of the element?
10. An unknown element (Z) is a dull, brittle powder that reacts with oxygen at high temperatures. Reaction of 0.665 gram of Z with oxygen under two different sets of conditions forms gaseous products with masses of 1.328 g and 1.660 g. To which family of elements does Z belong? What is the atomic mass of the element?
11. Why are the alkali metals such powerful reductants? Would you expect Li to be able to reduce $H_2$? Would Li reduce V? Why or why not?
12. What do you predict to be the most common oxidation state for Au, Sc, Ag, and Zn? Give the valence electron configuration for each element in its most stable oxidation state.
13. Complete the following table.

| | Mg | C | Ne | Fe | Br |
|---|---|---|---|---|---|
| Valence Electron Configuration | | | | | |
| Common Oxidation States | | | | | |
| Oxidizing Strength | | | | | |

14. Use the following information to identify elements T, X, D, and Z. Element T reacts with oxygen to form at least three compounds: TO, $T_2O_3$, and $TO_2$. Element X reacts with oxygen to form $XO_2$, but X is also known to form compounds in the +2 oxidation state. Element D forms $D_2O_3$, and element Z reacts vigorously and forms $Z_2O$. Electrical conductivity measurements showed that element X exhibited electrical conductivity intermediate between metals and insulators, while elements T, D, and Z were good conductors of electricity. Element T is a hard, lustrous, silvery metal, element X is a blue-gray metal, element D is a light, silvery metal, and element Z is a soft, low-melting metal.
15. Predict whether Cs, $F_2$, Al, and He will react with oxygen. If a reaction will occur, identify the products.
16. Predict whether K, Ar, O, and Al will react with $Cl_2$. If a reaction will occur, identify the products.
17. Use the following information to identify elements X, T, and Z.
    1. Element X is a soft, silvery-white metal that is flammable in air and reacts vigorously with water. Its first ionization energy is less than 500 kJ/mol, but the second ionization energy is greater than 3000 kJ/mol.
    2. Element T is a gas that reacts with $F_2$ to form a series of fluorides ranging from $TF_2$ to $TF_6$. It is inert to most other chemicals.
    3. Element Z is a deep red liquid that reacts with fluorine to form $ZF_3$ and with chlorine to form ZCl and $ZCl_3$, and with iodine to form ZI. Element Z also reacts with the alkali metals and alkaline earth metals.
18. Adding a reactive metal to water in the presence of oxygen results in a fire. In the absence of oxygen, the addition of 551 mg of the metal to water produces 6.4 mg of hydrogen gas. Treatment of 2.00 g of this metal with 6.3 g of $Br_2$ results in the formation of 3.86 g of an ionic solid. To which chemical family does this element belong? What is the identity of the element? Write and balance the chemical equation for the reaction of water with the metal to form hydrogen gas.

## Answers

1. $2\ Xe + 3\ O_2 \rightarrow 2\ XeO_3$

   The oxidation state of xenon in $XeO_3$ is +6. No, Ar is much more difficult to oxidize than Xe.

2.

3. The valence electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$. Its common oxidation states are: +6, due to loss of all six electrons in the 4*s* and 4*p* subshells; +4, due to loss of only the four 4*p* electrons; and −2, due to addition of two electrons to give an $[Ar]4s^2 3d^{10} 4p^6$ electron configuration, which is isoelectronic with the following noble gas, Kr. The highest oxidation state (+6) will be stabilized by bonds to highly electronegative atoms such as F ($SeF_6$) and O ($SeO_3$), while the lowest oxidation state will be stabilized in covalent compounds by bonds to less electronegative atoms such as H ($H_2Se$) or C [$(CH_3)_2Se$], or in ionic compounds with cations of electropositive metals ($Na_2Se$).

4.

5. All of the pnicogens have $ns^2np^3$ valence electron configurations. The pnicogens therefore tend to form compounds in three oxidation states: +5, due to loss of all five valence electrons; +3, due to loss of the three $np^3$ electrons; and −3, due to addition of three electrons to give a closed shell electron configuration. Bonds to highly electronegative atoms such as F and O will stabilize the higher oxidation states, while bonds to less electronegative atoms such as H and C will stabilize the lowest oxidation state, as will formation of an ionic compound with the cations of electropositive metals. The most common oxidation state for phosphorus and arsenic is +5.

6.

7. Uuq = *eka*-lead

8.

9. The ratios of the masses of the element to the mass of oxygen give empirical formulas of ZO, $Z_2O_3$, and $ZO_2$. The high electrical conductivity of the element immediately identifies it as a metal, and the existence of three oxides of the element with oxidation states separated by only one electron identifies it as a transition metal. If 1 g of Z reacts with 0.33 g $O_2$ to give ZO, the balanced equation for the reaction must be $2\ Z + O_2 \rightarrow 2\ ZO$. Using M to represent molar mass, the ratio of the molar masses of ZO and Z is therefore:

   $M_{ZO}:M_Z = (M_Z + M_O): M_Z = (M_Z + 16.0): M_Z = 1.33:1 = 1.33$.

   Solving for $M_Z$ gives a molar mass of 48 g/mol and an atomic mass of 48 amu for Z, which identifies it as titanium.

10.

11. Alkali metals are powerful reductants because they have a strong tendency to lose their $ns^1$ valence electron, as reflected in their low first ionization energies and electronegativities. Lithium has a more positive electron affinity than hydrogen and a substantially lower first ionization energy, so we expect lithium to reduce hydrogen. Transition metals have low electron affinities and do not normally form compounds in negative oxidation states. Therefore, we do not expect lithium to reduce vanadium.

12.

13.

| | Mg | C | Ne | Fe | Br |
|---|---|---|---|---|---|
| Valence Electron Configuration | $3s^2$ | $2s^2 2p^2$ | $2s^2 2p^6$ | $4s^2 3d^6$ | $4s^2 4p^5$ |
| Common Oxidation States | +2 | −4, +4 | 0 | +2, +3 | −1, +1, +3, +5, +7 |
| Oxidizing Strength | None | Weak | None | None | Strong |

14.

15. $4\ Cs(s) + O_2(g) \rightarrow 2\ Cs_2O(s)$ $2\ F_2(g) + O_2(g) \rightarrow OF_2(g)$ $4\ Al(s) + 3\ O_2(g) \rightarrow 2\ Al_2O_3(s)$ $He + O_2(g) \rightarrow$ no reaction

16.

17. 1. sodium or potassium
    2. xenon
    3. bromine

18.

## Contributors

- Anonymous

Modified by Joshua Halpern

Alkalai Metals Video from Open University on YouTube

Alkaline Earth Metals Video from David Read on YouTube

Halogen Gas Videos from Open University on YouTube

Lanthanide Metal Videos from Open University on YouTube

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# 7.4: Trace Elements in Biological Systems

**Learning Objectives**

- To describe some of the roles of trace elements in biological systems.

Of the more than 100 known elements, approximately 28 are known to be **essential** for the growth of at least one biological species, and only 19 are essential to humans. What makes some elements essential to an organism and the rest nonessential? There are at least two reasons:

1. The element must have some unique chemical property that an organism can use to its advantage and without which it cannot survive.
2. Adequate amounts of the element must be available in the environment in an easily accessible form.

As you can see in Table 7.6, many of the elements that are abundant in Earth's crust are nevertheless not found in an easily accessible form (e.g., as ions dissolved in seawater). Instead, they tend to form insoluble oxides, hydroxides, or carbonate salts. Although silicon is the second most abundant element in Earth's crust, $SiO_2$ and many silicate minerals are insoluble, so they are not easily absorbed by living tissues. This is also the case for iron and aluminum, which form insoluble hydroxides. Many organisms have therefore developed elaborate strategies to obtain iron from their environment. In contrast, molybdenum and iodine, though not particularly abundant, are highly soluble—molybdenum as molybdate ($MoO_4^{2-}$) and iodine as iodide ($I^-$) and iodate ($IO_3^-$)—and thus are more abundant in seawater than iron. Not surprisingly, both molybdenum and iodine are used by many organisms.

Table 7.6 Relative Abundance of Some Essential Elements in Earth's Crust and Oceans

| Element* | Crust (ppm; average) | Seawater (mg/L = ppm) |
|---|---|---|
| **O** | 461,000 | 857,000 |
| Si | 282,000 | 2.2 |
| Al | 82,300 | 0.002 |
| **Fe** | 56,300 | 0.002 |
| **Ca** | 41,500 | 412 |
| **Na** | 23,600 | 10,800 |
| **Mg** | 23,300 | 1290 |
| **K** | 20,900 | 399 |
| **H** | 1400 | 108,000 |
| **P** | 1050 | 0.06 |
| **Mn** | 950 | 0.0002 |
| F | 585 | 1.3 |
| **S** | 350 | 905 |
| **C** | 200 | 28 |
| **Cl** | 145 | 19,400 |
| V | 120 | 0.0025 |
| Cr | 102 | 0.0003 |
| Ni | 84 | 0.00056 |
| **Zn** | 70 | 0.0049 |
| **Cu** | 60 | 0.00025 |
| **Co** | 25 | 0.00002 |
| Li | 20 | 0.18 |
| **N** | 19 | 0.5 |
| Br | 2.4 | 67.3 |
| **Mo** | 1.2 | 0.01 |
| **I** | 0.45 | 0.06 |
| **Se** | 0.05 | 0.0002 |

*Elements in boldface are known to be essential to humans.

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Fortunately, many of the elements essential to life are necessary in only small amounts. (Table 1.6 lists trace elements in humans.) Even so, elements that are present in trace amounts can exert large effects on the health of an organism. Such elements function as part of an amplification mechanism, in which a molecule containing a trace element is an essential part of a larger molecule that acts in turn to regulate the concentrations of other molecules, and so forth. The amplification mechanism enables small variations in the concentration of the trace element to have large biochemical effects.

Essential trace elements in mammals can have four general roles: (1) they can behave as macrominerals, (2) they can participate in the catalysis of group-transfer reactions, (3) they can participate in oxidation–reduction reactions, or (4) they can serve as structural components.

## Macrominerals

The macrominerals—Na, Mg, K, Ca, Cl, and P—are found in large amounts in biological tissues and are present as inorganic compounds, either dissolved or precipitated. All form monatomic ions ($Na^+$, $Mg^{2+}$, $K^+$, $Ca^{2+}$, $Cl^-$) except for phosphorus, which is found as the phosphate ion ($PO_4^{3-}$). Recall that calcium salts are used by many organisms as structural materials, such as in bone [hydroxyapatite, $Ca_5(PO_4)_3OH$]; calcium salts are also in sea shells and egg shells ($CaCO_3$), and they serve as a repository for $Ca^{2+}$ in plants (calcium oxalate).

The body fluids of all multicellular organisms contain relatively high concentrations of these ions. Some ions ($Na^+$, $Ca^{2+}$, and $Cl^-$) are located primarily in *extracellular* fluids such as blood plasma, whereas $K^+$, $Mg^{2+}$, and phosphate are located primarily in *intracellular* fluids. Substantial amounts of energy are required to selectively transport these ions across cell membranes. The selectivity of these ion pumps is based on differences in ionic radius (Section 7.2) and ionic charge.

Maintaining optimum levels of macrominerals is important because temporary changes in their concentration within a cell affect biological functions. For example, nerve impulse transmission requires a sudden, reversible increase in the amount of $Na^+$ that flows into the nerve cell. Similarly, when hormones bind to a cell, they can cause $Ca^{2+}$ ions to enter that cell. In a complex series of reactions, the $Ca^{2+}$ ions trigger events such as muscle contraction, the release of neurotransmitters, or the secretion of hormones. When people who exercise vigorously for long periods of time overhydrate with water, low blood salt levels can result in a condition known as *hyponatremia*, which causes nausea, fatigue, weakness, seizures, and even death. For this reason, athletes should hydrate with a sports drink containing salts, not just water.

## Group-Transfer Reactions

Trace metal ions also play crucial roles in many biological group-transfer reactions. In these reactions, a recognizable functional group, such as a phosphoryl unit ($-PO_3^-$), is transferred from one molecule to another. In this example,

Equation 7.18

a unit is transferred from an alkoxide ($RO^-$) to hydroxide ($OH^-$). To neutralize the negative charge on the molecule that is undergoing the reaction, many biological reactions of this type require the presence of metal ions, such as $Zn^{2+}$, $Mn^{2+}$, $Ca^{2+}$, or $Mg^{2+}$ and occasionally $Ni^{2+}$ or $Fe^{3+}$. The effectiveness of the metal ion depends largely on its charge and radius.

Zinc is an important component of enzymes that catalyze the hydrolysis of proteins, the addition of water to $CO_2$ to produce $HCO_3^-$ and $H^+$, and most of the reactions involved in DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) synthesis, repair, and replication. Consequently, zinc deficiency has serious adverse effects, including abnormal growth and sexual development and a loss of the sense of taste.

## Biological Oxidation–Reduction Reactions

A third important role of trace elements is to transfer electrons in biological oxidation–reduction reactions. Iron and copper, for example, are found in proteins and enzymes that participate in $O_2$ transport, the reduction of $O_2$, the oxidation of organic molecules, and the conversion of atmospheric $N_2$ to $NH_3$. These metals usually transfer one electron per metal ion by alternating between oxidation states, such as 3+/2+ (Fe) or 2+/1+ (Cu).

Because most transition metals have multiple oxidation states separated by only one electron, they are uniquely suited to transfer multiple electrons one at a time. Examples include molybdenum (+6/+5/+4), which is widely used for two-electron oxidation–reduction reactions, and cobalt (+3/+2/+1), which is found in vitamin $B_{12}$. In contrast, many of the *p*-block elements are well suited for transferring *two* electrons at once. Selenium (+4/+2), for example, is found in the enzyme that catalyzes the oxidation of glutathione (GSH) to its disulfide form (GSSG):

$$2\ GSH + H_2O_2 \rightarrow 2\ H_2O + GSSG$$

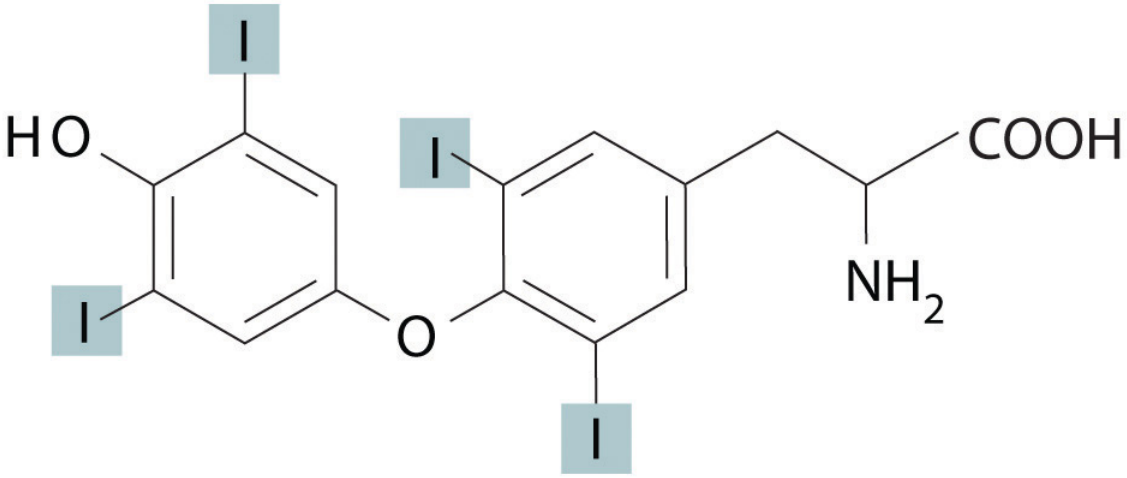
- ## Structural Components

  Trace elements also act as essential structural components of biological tissues or molecules. In many systems where trace elements do not change oxidation states or otherwise participate directly in biochemical reactions, it is often assumed, though frequently with no direct evidence, that the element stabilizes a particular three-dimensional structure of the biomolecule in which it is found. One example is a sugar-binding protein containing $Mn^{2+}$ and $Ca^{2+}$ that is a part of the biological defense system of certain plants. Other examples include enzymes that require $Zn^{2+}$ at one site for activity to occur at a different site on the molecule. Some nonmetallic elements, such as $F^-$, also appear to have structural roles. Fluoride, for example, displaces the hydroxide ion from hydroxyapatite in bone and teeth to form fluoroapatite [$Ca_5(PO_4)_3F$]. Fluoroapatite is less soluble in acid and provides increased resistance to tooth decay.

  Fluoroapatite ($Ca_5(PO_4)_3F$) is less soluble than hydroxyapatite ($Ca_5(PO_4)_3(OH)$)

  Another example of a nonmetal that plays a structural role is iodine, which in humans is found in only one molecule, the thyroid hormone *thyroxine*. When a person's diet does not contain sufficient iodine, the thyroid glands in their neck become greatly enlarged, leading to a condition called *goiter*. Because iodine is found primarily in ocean fish and seaweed, many of the original settlers of the American Midwest developed goiter due to the lack of seafood in their diet. Today most table salt contains small amounts of iodine [actually potassium iodide (KI)] to prevent this problem.




**Thyroxine**



**An individual with goiter.** In the United States, “iodized salt” prevents the occurrence of goiter.

### Example 9

There is some evidence that tin is an essential element in mammals. Based solely on what you know about the chemistry of tin and its position in the periodic table, predict a likely biological function for tin.

**Given:** element and data in Table 1.6

**Asked for:** likely biological function

**Strategy:**

From the position of tin in the periodic table, its common oxidation states, and the data in Table 1.6, predict a likely biological function for the element.

**Solution:**

From its position in the lower part of group 14, we know that tin is a metallic element whose most common oxidation states are +4 and +2. Given the low levels of tin in mammals (140 mg/70 kg human), tin is unlikely to function as a macromineral. Although a role in catalyzing group-transfer reactions or as an essential structural component cannot be ruled out, the most likely role for tin would be in catalyzing oxidation–reduction reactions that involve two-electron transfers. This would take advantage of the ability of tin to have two oxidation states separated by two electrons.

Exercise

Based solely on what you know about the chemistry of vanadium and its position in the periodic table, predict a likely biological function for vanadium.

**Answer:** Vanadium likely catalyzes oxidation–reduction reactions because it is a first-row transition metal and is likely to have multiple oxidation states.

### Summary

Many of the elements in the periodic table are **essential trace elements** that are required for the growth of most organisms. Although they are present in only small quantities, they have important biological effects because of their participation in an **amplification mechanism**. **Macrominerals** are present in larger amounts and play structural roles or act as electrolytes whose distribution in cells is tightly controlled. These ions are selectively transported across cell membranes by **ion pumps**. Other trace elements catalyze **group-transfer reactions** or biological oxidation–reduction reactions, while others yet are essential structural components of biological molecules.

### Key Takeaway

- Essential trace elements in mammals have four general roles: as macrominerals, as catalysts in group-transfer reactions or redox reactions, or as structural components.

### Conceptual Problems

1. Give at least one criterion for essential elements involved in biological oxidation–reduction reactions. Which region of the periodic table contains elements that are very well suited for this role? Explain your reasoning.
2. What are the general biological roles of trace elements that do not have two or more accessible oxidation states?

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# CHAPTER OVERVIEW

## 8: Ionic versus Covalent Bonding


8.1: What is a Chemical Bond?
8.2: Ionic Bonding
8.3: Lattice Energies in Ionic Solids
8.4: Lewis Electron Dot Symbols
8.5: Lewis Structures
8.6: Exceptions to the Octet Rule
8.7: Lewis Acids and Bases
8.8: Properties of Covalent Bonds
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# 8.1: What is a Chemical Bond?

**Learning Objectives**

- To present three common features of chemical bonding

A **chemical bond** is the force that holds atoms together in a chemical compound. There are three idealized types of bonding: covalent bondingA type of chemical bonding in which electrons are shared between atoms in a molecule or polyatomic ion., in which electrons are shared between atoms in a molecule or polyatomic ion, ionic bondingA type of chemical bonding in which positively and negatively charged ions are held together by electrostatic forces., in which positively and negatively charged ions are held together by electrostatic forces and **metallic bonding**, where all of the atoms in the metal share a few of their electrons which are free to circulate. One can relate the properties of materials to the type of bonding. Ionic compounds, for example, typically dissolve in water to form aqueous solutions that conduct electricity as the ions separate into solution. Solid ionic compounds do not conduct eletricity or heat. In contrast, most covalent compounds that dissolve in water form solutions that do not conduct electricity because they go into the solvent as neutral molecules. The solids or liquids are not conductors. In metals, of course, the free electrons conduct electricity, and what is not obvious, also heat. Metals are good conductors of both. Further, in general, covalent compounds are volatile because the forces holding the neutral molecules together are relatively weak, whereas ionic compounds are not because the individual ions are strongly attracted to each other.

Despite the differences in the distribution of electrons between these idealized types of bonding, all models of chemical bonding have three features in common:

1. Atoms interact with one another to form aggregates such as molecules, compounds, and crystals because doing so lowers the total energy of the system; that is, the aggregates are more stable than the isolated atoms.
2. The type of bonding is determined by how the outermost electrons of an atom, the so called **valence** electrons of one atom interact with neighboring atoms. In ionic materials electrons are fully transferred. Covalent materials share electrons with neighboring atoms and metals share electrons over a wide region.
3. Energy is required to dissociate bonded atoms or ions into isolated atoms or ions. For ionic solids, in which the ions form a three-dimensional array called a *lattice*, this energy is called the lattice energyThe enthalpy change that occurs when a solid ionic compound (whose ions form a three-dimensional array called a lattice) is transformed into gaseous ions., the change that occurs when a solid ionic compound is transformed into gaseous ions. For covalent compounds, this energy is called the bond energyThe enthalpy change that occurs when a given bond in a gaseous molecule is broken., which is the change that occurs when a given bond in a gaseous molecule is broken. The details of these processes will be discussed at the end of this semester when we study thermochemistry.
4. Each chemical bond is characterized by a particular optimal internuclear distance called the bond distance($r_0$)The optimal internuclear distance between two bonded atoms.. 

## Note the Pattern

Energy is required to dissociate bonded atoms or ions.

We explore these characteristics further, after briefly describing the energetic factors involved in the formation of an ionic bond.

## Summary

*Chemical bonding* is the general term used to describe the forces that hold atoms together in molecules and ions. Three idealized types of bonding are **ionic bonding**, in which positively and negatively charged ions are held together by electrostatic forces, **covalent bonding**, in which electron pairs are shared between atoms and metallic bonding where electrons are shared across large volumes of metal atoms ionic cores. All models of chemical bonding have three common features: atoms form bonds because the products are more stable than the isolated atoms; bonding interactions are characterized by a particular energy (the **bond energy** or **lattice energy**), which is the amount of energy required to dissociate the substance into its components; and bonding interactions have an optimal internuclear distance, the **bond distance**.

## Key Takeaway

- Forming bonds lowers the total energy of the system, energy is required to dissociate bonded atoms or ions, and there is an optimal bond distance.

## Conceptual Problems

1. Describe the differences between covalent bonding and ionic bonding. Which best describes the bonding in $MgCl_2$ and $PF_5$?
2. What three features do all chemical bonds have in common?

## Contributors

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# 8.2: Ionic Bonding

**Learning Objectives**

- To quantitatively describe the energetic factors involved in the formation of an ionic bond

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. The energy of the electrostatic attraction ($E$), a measure of the force's strength, is inversely proportional to the internuclear distance between the charged particles ($r$):

$$E \propto \frac{Q_1 Q_2}{r} \qquad E = k\frac{Q_1 Q_2}{r}$$

where each ion's charge is represented by the symbol $Q$. The proportionality constant $k$ is equal to $2.31 \times 10^{-28}$ J·m.This value of $k$ includes the charge of a single electron ($1.6022 \times 10^{-19}$ C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, $k$, equals 8.999 × 109 J·m/C$^2$. In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C). If $Q_1$ and $Q_2$ have opposite signs (as in NaCl, for example, where $Q_1$ is +1 for $Na^+$ and $Q_2$ is −1 for $Cl^-$), then $E$ is negative, which means that energy is released when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

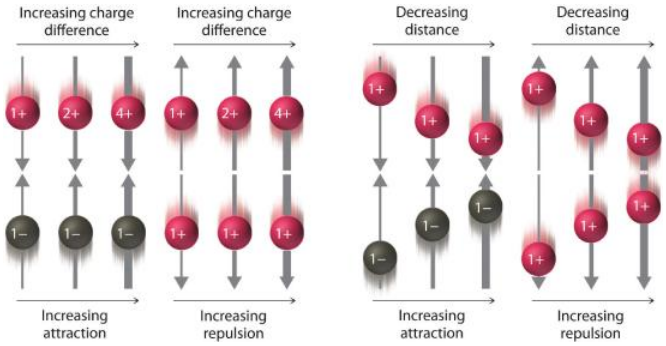



Figure 4.1.1 The Effect of Charge and Distance on the Strength of Electrostatic **Interactions.** *As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (−…+) or repulsive (−…− or +…+) interactions. The strength of these interactions is represented by the thickness of the arrows.*

For ions of opposite charge attraction increases as the charge increases and decreases as the distance between the ions increases

As shown by the green curve in the lower half of Figure 4.1.2 predicts that the maximum energy is released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure 4.1.2. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure 4.1.2 shows that the total energy of the system reaches a minimum at $r_0$, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured bond distance.

### Note the Pattern

Energy is released when a bond is formed.

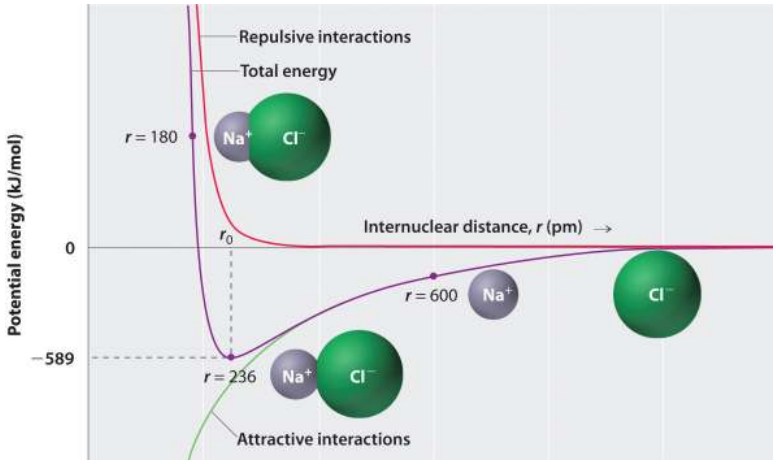
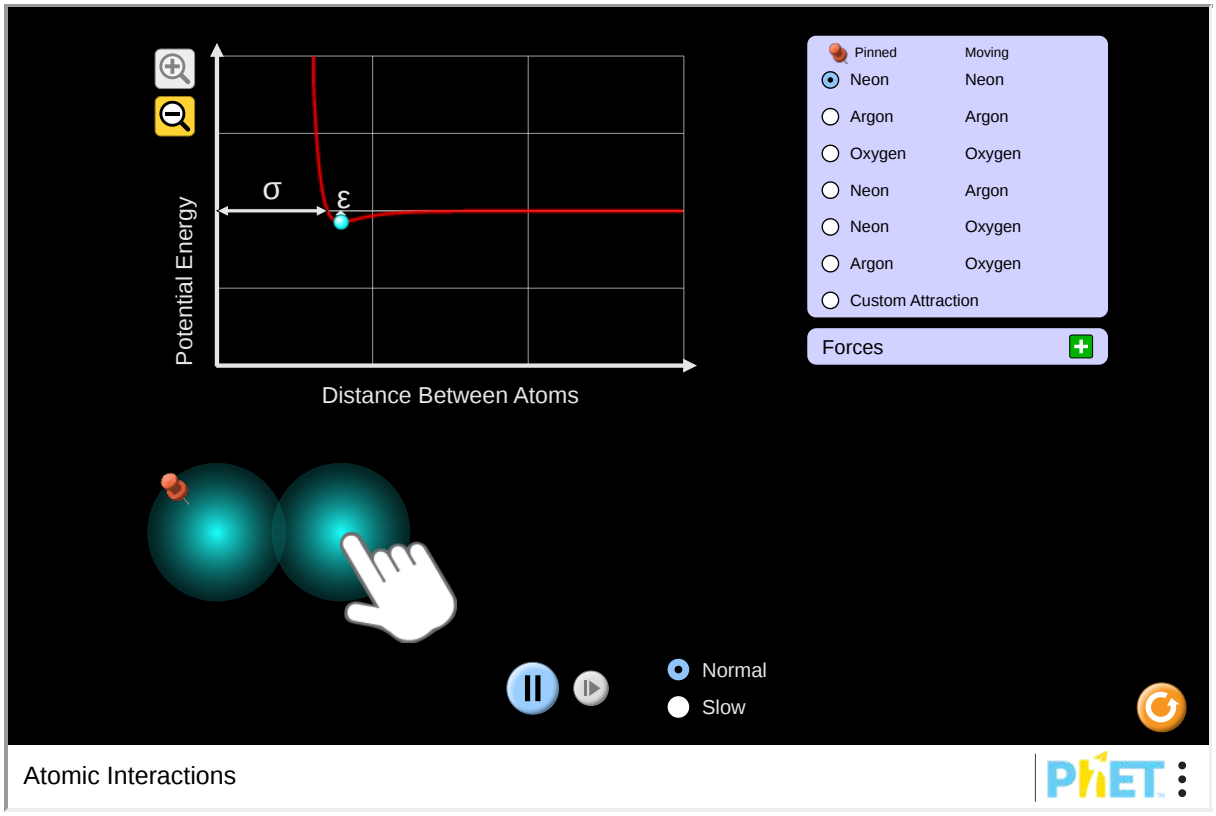



Figure 4.1.2 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Ions With Different Charges: A Gaseous $Na^+$ Ion and a Gaseous $Cl^-$ **Ion** *The energy of the system reaches a minimum at a particular distance ($r_0$) when the attractive and repulsive interactions are balanced. Below is an app from pHet which illustrates the same point for neutral atoms. You can move the unpinned atom with respect to the pinned one by dragging it and you can see where on the potential curve you are as a function of the distance between them. The major difference between the curves for the ionic attraction and the neutral atoms is that the force between the ions is much stronger and thus the depth of the well much deeper, We will revisit this app when we talk about bonds that are not ionic.*




Let's consider the energy released when a gaseous $Na^+$ ion and a gaseous $Cl^-$ ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+(g)$ ion and a $Cl^-(g)$ ion is as follows:

$$E = k\frac{Q_1Q_2}{r_0} = (2.31 \times 10^{-28}\text{J} \cdot \cancel{\text{m}}) \left( \frac{(+1)(-1)}{236\ \cancel{\text{pm}} \times 10^{-12}\ \cancel{\text{m/pm}}} \right) = -9.79 \times 10^{-19}\ \text{J/ion pair}$$

The negative value indicates that energy is released. Our convention is that if a chemcal process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive, energy has to be given to the atoms. To

calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = \left(-9.79 \times 10^{-19}\ J/\cancel{ion pair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\ pair}/mol\right) = -589\ kJ/mol$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the lattice energy of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At $r_0$, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at $r_0$, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

## Ionic Crystal Lattices

An ionic solid is formed out of endlessly repeating patterns of ionic pairs. Because we want to establish the basics about ionic bonding and not get involved in detail we will continue to use table salt, NaCl, to discuss ionic bonding.

In NaCl, of course, an electron is transferred from each sodium atom to a chlorine atom leaving $Na^+$ and $Cl^-$. The size of the lattice depends on the physical size of the crystal which can be microscopic, a few nm on a side to macroscopic, centimeters or even more. Salt crystals that you buy at the store can range in size from a few tenths of a mm in finely ground table salt to a few mm for coarsely ground salt used in cooking. Given that the spacing between the $Na^+$ and $Cl^-$ ions, is ~240 pm, a 2.4 mm on edge crystal has $10^{+7}$ $Na^+$ - $Cl^-$ units, and a cube of salt 2mm on edge will have about 2 x $10^{21}$ atoms.

The ions arrange themselves into an extended lattice. The distinguishing feature of these lattices is that they are space filling, there are no voids. Thinking about this in three dimensions this turns out to be a bit complex. In nature, there are only 14 such lattices, called Bravais lattices after August Bravais who first classified them in 1850. If interested, you can view a video visualization of the 14 lattices by Manuel Moreira Baptista

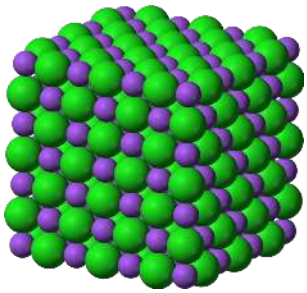


Figure 4.1.3 Small section of the arrangement of ions in an NaCl **crystal.** *The relative positions of the sodium ions are shown in blue, the chlorine in green*

Remember that the $Na^+$ ions, shown here in purple, will be much smaller than Na atoms, and $Cl^-$ ions will be much larger than Cl atoms. The repeating pattern is called the unit cell.

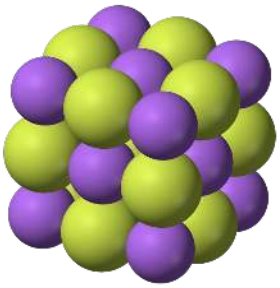


**Figure 4.1.4The unit cell for an NaCl crystal lattice.** *If you look at the diagram carefully, you will see that the sodium ions and chloride ions alternate with each other in each of the three dimensions.*

This diagram is easy enough to draw with a computer, but extremely difficult to draw convincingly by hand. We normally draw an "exploded" version which looks like this:

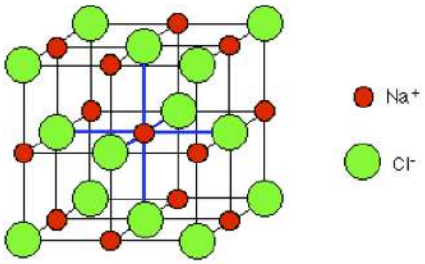



Figure 4.1.5 An "exploded" view of the unit cell for an NaCl crystal lattice. *The sodium ion in the center is being touched by 6 chloride ions as indicated by the blue lines.*

By chance we might just as well have centered the diagram around a chloride ion - that, of course, would be touched by 6 sodium ions. Sodium chloride is described as being 6:6-coordinated. This diagram represents only a tiny part of the whole sodium chloride crystal; the pattern repeats in this way over countless ions.

## Sodium chloride has a high melting and boiling point

There are strong electrostatic attractions between the positive and negative ions, and it takes a lot of heat energy to overcome them. Ionic substances all have high melting and boiling points. Differences between ionic substances will depend on things like:

- **The number of charges on the ions**: Magnesium oxide has exactly the same structure as sodium chloride, but a much higher melting and boiling point. The 2+ and 2- ions attract each other more strongly than 1+ attracts 1-.
- **The sizes of the ions**: If the ions are smaller they get closer together and so the electrostatic attractions are greater. Rubidium iodide, for example, melts and boils at slightly lower temperatures than sodium chloride, because both rubidium and iodide ions are bigger than sodium and chloride ions. The attractions are less between the bigger ions and so less heat energy is needed to separate them.

## Sodium chloride crystals are brittle

Brittleness is again typical of ionic substances. Imagine what happens to the crystal if a stress is applied which shifts the ion layers slightly.

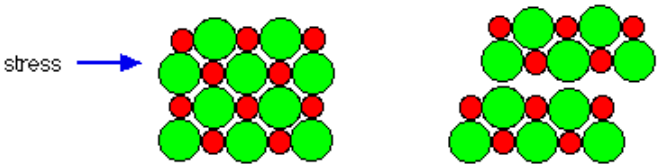



Figure 4.1.5 Cleaving an ionic crystal. *When an ionic crystal is cleeved, a sharp tool such as a knife, displaces adjourning layers of the crystal, pushing ions of the same charge on top of each other. At that point the two pieces repel each other, shattering the crystal.*

## The electrical behavior of sodium chloride

Solid sodium chloride does not conduct electricity, because there are no electrons which are free to move. When it melts, at a very high temperature of course, the sodium and chloride ions can move freely when a voltage is placed across the liquid. The positive sodium ions move towards the negatively charged electrode (the cathode). When they get there, each sodium ion picks up an electron from the electrode to form a sodium atom. These float to the top of the melt as molten sodium metal. (And assuming you are doing this open to the air, this immediately catches fire and burns with an orange flame.)

The power source (the battery or whatever) moves electrons along the wire in the external circuit so that the number of electrons is the same. That flow of electrons would be seen as an electric current (the external circuit is all the rest of the circuit apart from the

molten sodium chloride.) Thus, in the process called electrolysis, sodium and chlorine are produced. This is a chemical change rather than a physical process.

$$Na^+ + e^- \rightarrow Na$$

Meanwhile, chloride ions are attracted to the positive electrode (the anode). When they get there, each chloride ion loses an electron to the anode to form an atom. These then pair up to make chlorine molecules. Chlorine gas is produced. Overall, the change is . . .

$$2Cl^- \rightarrow Cl)2 + 2e^-$$

The new electrons deposited on the anode are pumped off around the external circuit by the power source, eventually ending up on the cathode where they will be transferred to sodium ions. Molten sodium chloride conducts electricity because of the movement of the ions in the melt, and the discharge of the ions at the electrodes. Both of these have to happen if you are to get electrons flowing in the external circuit. In solid sodium chloride, of course, that ion movement can not happen and that stops any possibility of any current flow in the circuit.

Acknowlegement: The discussion of the NaCl lattice is a slightly modified version of the Jim Clark's article on the ChemWiki

## Example 1

Calculate the amount of energy released when 1 mol of gaseous $Li^+F^-$ ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

**Given:** cation and anion, amount, and internuclear distance

**Asked for:** energy released from formation of gaseous ion pairs

**Strategy:**

Substitute the appropriate values into Equation 4.1.1 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

**Solution:**

Inserting the values for $Li^+F^-$ into Equation 4.1.1 (where $Q_1$ = +1, $Q_2$ = −1, and $r$ = 156 pm), we find that the energy associated with the formation of a single pair of $Li^+F^-$ ions is

$$E = k\frac{Q_1Q_2}{r_0} = (2.31 \times 10^{-28}\text{J} \cdot \cancel{\text{m}}) \left( \frac{(+1)(-1)}{156\ \cancel{\text{pm}} \times 10^{-12}\ \cancel{\text{m/pm}}} \right) = -1.48 \times 10^{-18}\ \text{J/ion pair}$$

Then the energy released per mole of $Li^+F^-$ ion pairs is

$$E = \left(-1.48 \times 10^{-18}\ J/\cancel{ion pair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\ pair}/mol\right) = -891\ kJ/mol$$

Because $Li^+$ and $F^-$ are smaller than $Na^+$ and $Cl^-$ (see  Figure 3.2.7 ), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 4.1.1, much more energy is released when 1 mol of gaseous $Li^+F^-$ ion pairs is formed (−891 kJ/mol) than when 1 mol of gaseous $Na^+Cl^-$ ion pairs is formed (−589 kJ/mol).

Exercise

Calculate the amount of energy released when 1 mol of gaseous MgO ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

**Answer:** −3180 kJ/mol = $-3.18 \times 10^3$ kJ/mol

## Summary

The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Ionic compounds usually form hard crystalline solids that melt at rather high temperatures and are *very* resistant to evaporation. They can be easily cleaved. When the dissolve in aqueous solution, the ions make the solution a good conductor of electricity.

These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in part (a) in Figure 4.1.5 , which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions.

## Key Takeaway

- The amount of energy needed to separate a gaseous ion pair is its bond energy.

## Conceptual Problems

1. Describe the differences in behavior between NaOH and $CH_3OH$ in aqueous solution. Which solution would be a better conductor of electricity? Explain your reasoning.
2. What is the relationship between the strength of the electrostatic attraction between oppositely charged ions and the distance between the ions? How does the strength of the electrostatic interactions change as the size of the ions increases?
3. Which will result in the release of more energy: the interaction of a gaseous sodium ion with a gaseous oxide ion or the interaction of a gaseous sodium ion with a gaseous bromide ion? Why?
4. Which will result in the release of more energy: the interaction of a gaseous chloride ion with a gaseous sodium ion or a gaseous potassium ion? Explain your answer.
5. What are the predominant interactions when oppositely charged ions are
    1. far apart?
    2. at internuclear distances close to $r_0$?
    3. very close together (at a distance that is *less* than the sum of the ionic radii)?
6. Several factors contribute to the stability of ionic compounds. Describe one type of interaction that *destabilizes* ionic compounds. Describe the interactions that *stabilize* ionic compounds.
7. What is the relationship between the electrostatic attractive energy between charged particles and the distance between the particles?

## Answer

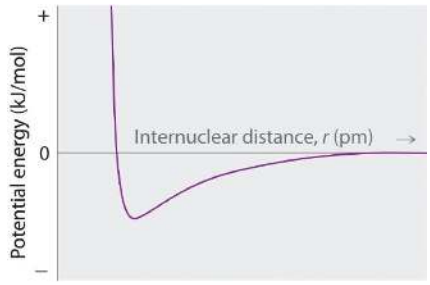
1.
2.
3. The interaction of a sodium ion and an oxide ion. The electrostatic attraction energy between ions of opposite charge is directly proportional to the charge on each ion ($Q_1$ and $Q_2$ in Equation 4.1.1). Thus, more energy is released as the charge on the ions increases (assuming the internuclear distance does not increase substantially). A sodium ion has a +1 charge; an oxide ion, a −2 charge; and a bromide ion, a −1 charge. For the interaction of a sodium ion with an oxide ion, $Q_1 = +1$ and $Q_2 = −2$, whereas for the interaction of a sodium ion with a bromide ion, $Q_1 = +1$ and $Q_2 = −1$. The larger value of $Q_1 \times Q_2$ for the sodium ion–oxide ion interaction means it will release more energy.
4.
5.
6.
7.

## Numerical Problems

1. How does the energy of the electrostatic interaction between ions with charges +1 and −1 compare to the interaction between ions with charges +3 and −1 if the distance between the ions is the same in both cases? How does this compare with the magnitude of the interaction between ions with +3 and −3 charges?
2. How many grams of gaseous $MgCl_2$ are needed to give the same electrostatic attractive energy as 0.5 mol of gaseous LiCl? The ionic radii are $Li^+$ = 76 pm, $Mg^{+2}$ = 72 pm, and $Cl^-$ = 181 pm.
3. Sketch a diagram showing the relationship between potential energy and internuclear distance (from $r = \infty$ to $r = 0$) for the interaction of a bromide ion and a potassium ion to form gaseous KBr. Explain why the energy of the system increases as the distance between the ions decreases from $r = r_0$ to $r = 0$.

4. Calculate the magnitude of the electrostatic attractive energy ($E$, in kilojoules) for 85.0 g of gaseous SrS ion pairs. The observed internuclear distance in the gas phase is 244.05 pm.
5. What is the electrostatic attractive energy ($E$, in kilojoules) for 130 g of gaseous $HgI_2$? The internuclear distance is 255.3 pm.

## Answers

1. According to Equation 4.1.1, in the first case $Q_1Q_2 = (+1)(-1) = -1$; in the second case, $Q_1Q_2 = (+3)(-1) = -3$. Thus, $E$ will be three times larger for the +3/−1 ions. For +3/−3 ions, $Q_1Q_2 = (+3)(-3) = -9$, so $E$ will be nine times larger than for the +1/−1 ions.
2. 
3. 


   At $r < r_0$, the energy of the system increases due to electron–electron repulsions between the overlapping electron distributions on *adjacent* ions. At very short internuclear distances, electrostatic repulsions between adjacent *nuclei* also become important.
4. 
5. 

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Diatomic Molecule Simulation from pHet

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# 8.3: Lattice Energies in Ionic Solids

**Learning Objectives**

- To understand the relationship between the lattice energy and physical properties of an ionic compound

The reaction of a metal with a nonmetal usually produces an ionic compound; that is, electrons are transferred from the metal to the nonmetal. Metal ores are commonly combinations of metal atoms with oxygen atoms, and this combination is produced when metals rust, so the process where electrons are transferred to the oxygen atoms from the metal atoms is known as **oxidation** of the metal and the reverse process, where pure metals are produced is called **reduction** of the ore to the metal.

Ionic compounds are usually rigid, brittle, crystalline substances with flat surfaces that intersect at characteristic angles. They are not easily deformed, and they melt at relatively high temperatures. NaCl, for example, melts at 801°C. These properties result from the regular arrangement of the ions in the crystalline lattice and from the strong electrostatic attractive forces between ions with opposite charges.

While Equation 4.1.1 has demonstrated that the formation of ion pairs from isolated ions releases large amounts of energy, even more energy is released when these ion pairs condense to form an ordered three-dimensional array. In such an arrangement each cation in the lattice is surrounded by more than one anion (typically four, six, or eight) and vice versa, so it is more stable than a system consisting of separate pairs of ions, in which there is only one cation–anion interaction in each pair. Note that $r_0$ may differ between the gas-phase dimer and the lattice.

### Note the Pattern

An ionic lattice is more stable than a system consisting of separate ion pairs.

## Calculating Lattice Energies

The lattice energy of nearly any ionic solid can be calculated rather accurately using a modified form of Equation 4.1:

$$U = -k' \frac{Q_1 Q_2}{r_0}, \; where \; U > 0$$

$U$, which is always a positive number, represents the amount of energy required to dissociate 1 mol of an ionic solid into the gaseous ions. As before, $Q_1$ and $Q_2$ are the charges on the ions and $r_0$ is the internuclear distance. We see from Equation 4.4 that lattice energy is directly related to the product of the ion charges and inversely related to the internuclear distance. The value of the constant $k'$ depends on the specific arrangement of ions in the solid lattice and their valence electron configurations, topics that will be discussed in more detail in the second semester. Representative values for calculated lattice energies, which range from about 600 to 10,000 kJ/mol, are listed in Table 4.2.1. Energies of this magnitude can be decisive in determining the chemistry of the elements.

**Table 4.2.1 Representative Calculated Lattice Energies**

| Substance | $U$ (kJ/mol) |
|---|---|
| NaI | 682 |
| $CaI_2$ | 1971 |
| $MgI_2$ | 2293 |
| NaOH | 887 |
| $Na_2O$ | 2481 |
| $NaNO_3$ | 755 |
| $Ca_3(PO_4)_2$ | 10,602 |
| $CaCO_3$ | 2804 |

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Because the lattice energy depends on the *product* of the charges of the ions, a salt having a metal cation with a +2 charge ($M^{2+}$) and a nonmetal anion with a −2 charge ($X^{2-}$) will have a lattice energy four times greater than one with $M^+$ and $X^-$, assuming the ions are of comparable size (and have similar internuclear distances). For example, the calculated value of $U$ for NaF is 910 kJ/mol, whereas $U$ for MgO (containing $Mg^{2+}$ and $O^{2-}$ ions) is 3795 kJ/mol.

Because lattice energy is *inversely* related to the internuclear distance, it is also inversely proportional to the size of the ions. This effect is illustrated in Figure 4.2.2, which shows that lattice energy decreases for the series LiX, NaX, and KX as the radius of $X^-$ increases. Because $r_0$ in Equation 4.2.1 is the sum of the ionic radii of the cation and the anion ($r_0 = r^+ + r^-$), $r_0$ increases as the cation becomes larger in the series, so the magnitude of $U$ decreases. A similar effect is seen when the anion becomes larger in a series of compounds with the same cation.

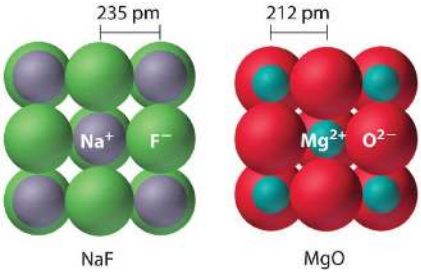



**Figure 4.2.1 Unit cells for NaF and MgO**

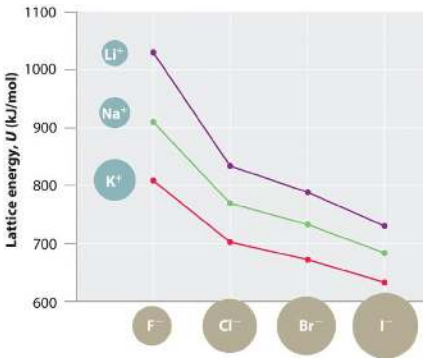



Figure 4.2.2 A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium **Halides.** *Because the ionic radii of the cations decrease in the order $K^+ > Na^+ > Li^+$ for a given halide ion, the lattice energy decreases smoothly from $Li^+$ to $K^+$. Conversely, for a given alkali metal ion, the fluoride salt always has the highest lattice energy and the iodide salt the lowest.*

## Note the Pattern

Lattice energies are highest for substances with small, highly charged ions.

## Example 2

Arrange GaP, BaS, CaO, and RbCl in order of increasing lattice energy.

**Given:** four compounds

**Asked for:** order of increasing lattice energy

**Strategy:**

Using Equation 4.2.1, predict the order of the lattice energies based on the charges on the ions. For compounds with ions with the same charge, use the relative sizes of the ions to make this prediction.

**Solution:**

The compound GaP, which is used in semiconductor electronics, contains $Ga^{3+}$ and $P^{3-}$ ions; the compound BaS contains $Ba^{2+}$ and $S^{2-}$ ions; the compound CaO contains $Ca^{2+}$ and $O^{2-}$ ions; and the compound RbCl has $Rb^+$ and $Cl^-$ ions. We know from Equation 4.4 that lattice energy is directly proportional to the product of the ionic charges. Consequently, we expect RbCl, with a (−1)(+1)

term in the numerator, to have the lowest lattice energy, and GaP, with a (+3)(−3) term, the highest. To decide whether BaS or CaO has the greater lattice energy, we need to consider the relative sizes of the ions because both compounds contain a +2 metal ion and a −2 chalcogenide ion. Because $Ba^{2+}$ lies below $Ca^{2+}$ in the periodic table, $Ba^{2+}$ is larger than $Ca^{2+}$. Similarly, $S^{2-}$ is larger than $O^{2-}$. Because the cation and the anion in BaS are both larger than the corresponding ions in CaO, the internuclear distance is greater in BaS and its lattice energy will be lower than that of CaO. The order of increasing lattice energy is RbCl < BaS < CaO < GaP.

Exercise

Arrange InAs, KBr, LiCl, SrSe, and ZnS in order of decreasing lattice energy.

**Answer:** InAs > ZnS > SrSe > LiCl > KBr

## The Relationship between Lattice Energies and Physical Properties

The magnitude of the forces that hold an ionic substance together has a dramatic effect on many of its properties. The melting point is the temperature at which the individual ions in a lattice or the individual molecules in a covalent compound have enough kinetic energy to overcome the attractive forces that hold them together in the solid. At the melting point, the ions can move freely, and the substance becomes a liquid. Thus melting points vary with lattice energies for ionic substances that have similar structures. The melting points of the sodium halides (Figure 4.2.3), for example, decrease smoothly from NaF to NaI, following the same trend as seen for their lattice energies (Figure 4.2.2). Similarly, the melting point of MgO is 2825°C, compared with 996°C for NaF, reflecting the higher lattice energies associated with higher charges on the ions. In fact, because of its high melting point, MgO is used as an electrical insulator in heating elements for electric stoves.

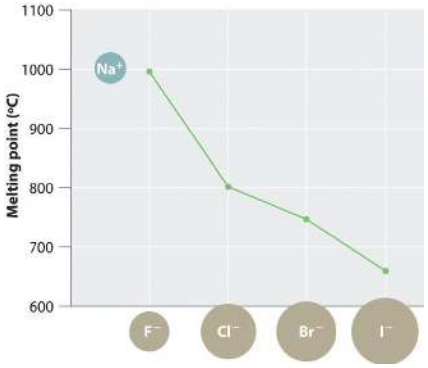



Figure 4.2.2.

The hardness s the resistance of ionic materials to scratching or abrasion. of ionic materials—that is, their resistance to scratching or abrasion—is also related to their lattice energies. Hardness is directly related to how tightly the ions are held together electrostatically, which, as we saw, is also reflected in the lattice energy. As an example, MgO is harder than NaF, which is consistent with its higher lattice energy.

In addition to determining melting point and hardness, lattice energies affect the solubilities of ionic substances in water. In general, *the higher the lattice energy, the less soluble a compound is in water*. For example, the solubility of NaF in water at 25°C is 4.13 g/100 mL, but under the same conditions, the solubility of MgO is only 0.65 mg/100 mL, meaning that it is essentially insoluble.

### Note the Pattern

High lattice energies lead to hard, insoluble compounds with high melting points.

### Summary

Ionic compounds have strong electrostatic attractions between oppositely charged ions in a regular array. The lattice energy ($U$) of an ionic substance is defined as the energy required to dissociate the solid into gaseous ions; $U$ can be calculated from the charges on the ions, the arrangement of the ions in the solid, and the internuclear distance. Because $U$ depends on the product of the ionic charges, substances with di- or tripositive cations and/or di- or trinegative anions tend to have higher lattice energies than their singly charged counterparts. Higher lattice energies typically result in higher **melting points** and increased **hardness** because more thermal energy is needed to overcome the forces that hold the ions together.

## Key Takeaway

- The lattice energy is usually the most important energy factor in determining the stability of an ionic compound.

## Key Equation

**Lattice energy**

$$U = -k' \frac{Q_1 Q_2}{r_0} \tag{4.2.1}$$

## Conceptual Problems

1. If a great deal of energy is required to form gaseous ions, why do ionic compounds form at all?
2. What are the general physical characteristics of ionic compounds?
3. Ionic compounds consist of crystalline lattices rather than discrete ion pairs. Why?
4. What factors affect the magnitude of the lattice energy of an ionic compound? What is the relationship between ionic size and lattice energy?
5. Which would have the larger lattice energy—an ionic compound consisting of a large cation and a large anion or one consisting of a large anion and a small cation? Explain your answer and any assumptions you made.
6. How would the lattice energy of an ionic compound consisting of a monovalent cation and a divalent anion compare with the lattice energy of an ionic compound containing a monovalent cation and a monovalent anion, if the internuclear distance was the same in both compounds? Explain your answer.
7. Which would have the larger lattice energy—$CrCl_2$ or $CrCl_3$—assuming similar arrangements of ions in the lattice? Explain your answer.
8. Which cation in each pair would be expected to form a chloride salt with the larger lattice energy, assuming similar arrangements of ions in the lattice? Explain your reasoning.
    1. $Na^+$, $Mg^{2+}$
    2. $Li^+$, $Cs^+$
    3. $Cu^+$, $Cu^{2+}$
9. Which cation in each pair would be expected to form an oxide with the higher melting point, assuming similar arrangements of ions in the lattice? Explain your reasoning.
    1. $Mg^{2+}$, $Sr^{2+}$
    2. $Cs^+$, $Ba^{2+}$
    3. $Fe^{2+}$, $Fe^{3+}$

## Numerical Problems

1. Arrange SrO, PbS, and $PrI_3$ in order of decreasing lattice energy.
2. Compare BaO and MgO with respect to each of the following properties.
    1. enthalpy of sublimation
    2. ionization energy of the metal
    3. lattice energy
    4. enthalpy of formation
3. 

## Contributors

- Anonymous

Modified by Joshua Halpern (Howard University)

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# 8.4: Lewis Electron Dot Symbols

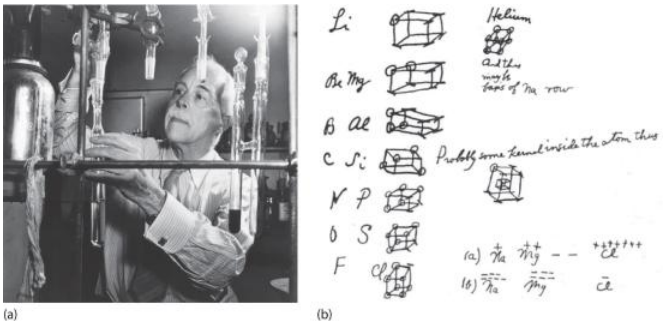
**Learning Objectives**

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbolsA system that can be used to predict the number of bonds formed by most elements in their compounds., often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds (Figure 5.2.1). Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons, the total number of *s* and *p* electrons in the outermost shell available for bonding. Lewis symbols do not easily capture the involvement of *d* electrons in bonding, but are incredibly useful for describing bonding of the first three periods and indicating which atoms are bonded to which ones. They are how organic molecular structures are drawn. As a simple example, Cesium, has the electron configuration $[Xe]6s^1$, which indicates one valence electron outside a closed shell. In the Lewis dot symbol, this single electron is represented as a single dot:



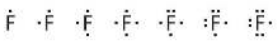

**Figure 5.2.1 G. N. Lewis and the Octet Rule**




*(a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.*

## Creating a Lewis Dot Symbol

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. Fluorine, for example, with the electron configuration $[He]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 4.3.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 4.3.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

**Figure 5.2.2 Lewis Dot Symbols for the Elements in Period 2**

| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| Electron Configuration | $[He]2s^1$ | $[He]2s^2$ | $[He]2s^22p^1$ | $[He]2s^22p^2$ | $[He]2s^22p^3$ | $[He]2s^22p^4$ | $[He]2s^22p^5$ | $[He]2s^22p^6$ |
| Lewis Dot Symbol | Li· | ·Be· | ·Ḃ· | ·Ċ· | ·N̈· | :Ö· | :F̈· | :N̈e: |

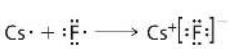
## The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule The tendency for atoms to lose, gain, or share electrons to reach a total of eight valence electrons. explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to having one *ns* and three *np* valence orbitals filled, which together can accommodate a total of eight electrons. We also know that the configuration $ns^2np^6$ is the one in a period which with the highest ionization energy and the lowest electron affinity. This level is the most difficult to take a valence electron away from or add one to. Atoms which can achieve an $ns^2np^6$ by sharing, borrowing or lending electrons to another atom which also achieves this configuration in the exchange will form a bond.

Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom and more than two before Schrödinger had explained the electronic structure of hydrogen.

For some time helium was treated as an exception to the octet rule. Today we know that helium's $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, why gains its one electron to achieve the electron configuration of helium. We understand this as a consequence of only two electrons being able to fit in the $n = 1$ shell, in Lewis' time this was a mystery, something that was simply accepted. It is the ability to understand the atomic orbital basis of *ad hoc* rules developed in the past that motivates our atoms first approach to chemistry.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on $Cs^+$ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the $Cs^+$ ion, which has the valence electron configuration of Xe, and the $F^-$ ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement in Chapter 3 that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe in Section 4.5. These include molecules in which one or more atoms contain fewer or more than eight electrons. In Section 4.4 , however, we explain how to form molecular compounds by completing octets.

### Summary

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

### Key Takeaway

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

### Conceptual Problems

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?

2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?
4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom described in Chapter 2 ? How is it different?

## Answer

1.
2.
3. Lewis dot symbols allow us to predict the number of bonds atoms will form, and therefore the stoichiometry of a compound. The Lewis structure of a compound also indicates the presence or absence of lone pairs of electrons, which provides information on the compound's chemical reactivity and physical properties.
4.

## Contributors

- Anonymous

Modified by Joshua Halpern (Howard University)

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# 8.5: Lewis Structures

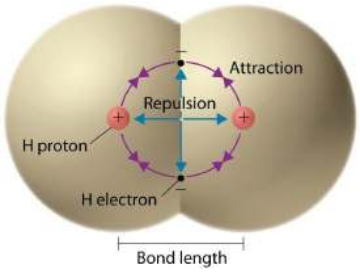
**Learning Objectives**

- To use Lewis dot symbols to explain the stoichiometry of a compound.
- To understand the concept of resonance.

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the $H_2$ molecule, which contains a purely covalent bond. Each hydrogen atom in $H_2$ contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 5.3.1):

- The electrons in the two atoms repel each other because they have the same charge ($E > 0$).
- Similarly, the protons in adjacent atoms repel each other ($E > 0$).
- The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$).Recall from Chapter 2 that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.

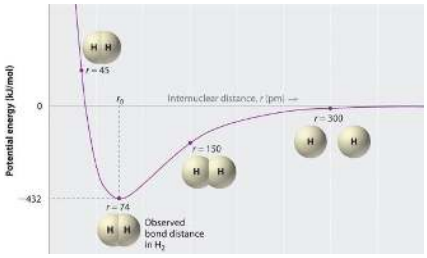
**Figure 5.3.1 Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule**




*Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.*

A plot of the potential energy of the system as a function of the internuclear distance (Figure 5.3.2 ) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in $H_2$ is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figure 5.3.2 and Figure 4.1.2 , which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

**Figure 5.3.2 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms**

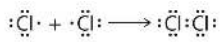



*At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the*

*internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.*

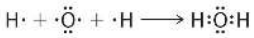
## Using Lewis Dot Symbols to Describe Covalent Bonding

This sharing of electrons allowing atoms to "stick" together is the basis of covalent bonding. There is some intermediate distant, generally a bit longer than 0.1 nm, or if you prefer 100 pm, at which the attractive forces significantly outweigh the repulsive forces and a bond will be formed if both atoms can achieve a completen $s^2np^6$ configuration. It is this behavior that Lewis captured in his octet rule. The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming $Cl_2$, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair A pair of electrons in a Lewis structure that is shared by two atoms, thus forming a covalent bond.; the other three pairs of electrons on each chlorine atom are called lone pairsA pair of electrons in a Lewis structure that is not involved in covalent bonding.. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bondA covalent bond in which both electrons come from the same atom.. Examples of this type of bonding are presented in Section 5.4 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for $H_2O$. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in $CCl_4$ and $CO_3^{2-}$, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

### Note the Pattern

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall from Chapter 2 that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For $CO_3^{2-}$, for example, we add two electrons to the total because of the −2 charge.

3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In $H_2O$, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.

5. **If any electrons are left over, place them on the central atom.** We explain in Section 4.6 that some atoms are able to accommodate more than eight electrons.

6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

## $H_2O$

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.

3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.

4. Each H atom has a full valence shell of 2 electrons.

5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

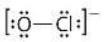
## $OCl^-$

1. With only two atoms in the molecule, there is no central atom.

2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.

3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.

4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. $OCl^-$ is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

## $CH_2O$

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

### Example 3

Write the Lewis electron structure for each species.

1. $NCl_3$
2. $S_2^{2-}$
3. NOCl

**Given:** chemical species

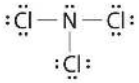
**Asked for:** Lewis electron structures

**Strategy:**

Use the six-step procedure to write the Lewis electron structure for each species.

**Solution:**

1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

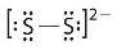


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

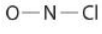


Nitrogen trichloride

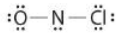
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



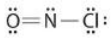
3. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



Nitrosyl chloride

Exercise

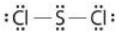
Write Lewis electron structures for $CO_2$ and $SCl_2$, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

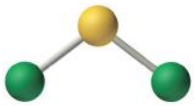
**Answer**

1. 



Carbon dioxide

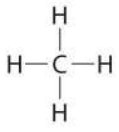
2. 



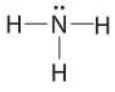
Sulfur dichloride

## Using Lewis Electron Structures to Explain Stoichiometry

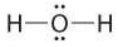
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of group 17 (the halogens), this number is one; for the elements of group 16 (the chalcogens), it is two; for group 15, three; and for group 14, four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Group 14



Group 15

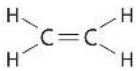


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



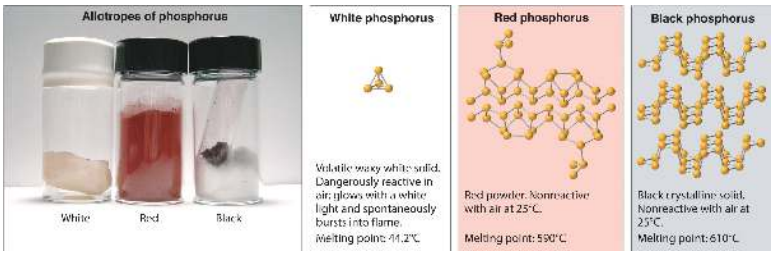
Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule. Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 5.1.3 ). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

### Note the Pattern

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

**Figure 5.3.3 The Three Allotropes of Phosphorus: White, Red, and Black**




*All three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains $P_4$ tetrahedra, red phosphorus is a network of linked $P_8$ and $P_9$ units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

## Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for $CH_2O$, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal chargeThe difference between the number of valence electrons in a free atom and the number of electrons assigned to it in a particular Lewis electron structure. on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

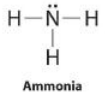
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia ($NH_3$) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding $e^-$ + (6 bonding $e^-$/2)]. Substituting into Equation 5.3.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding $e^-$ + (2 bonding $e^-$/2)]. Using Equation 4.4.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the $NH_3$ molecule.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

### Example 4

Calculate the formal charges on each atom in the $NH_4^+$ ion.

**Given:** chemical species

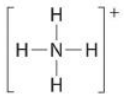
**Asked for:** formal charges

**Strategy:**

Identify the number of valence electrons in each atom in the $NH_4^+$ ion. Use the Lewis electron structure of $NH_4^+$ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 4.4.1 to calculate the formal charge on each atom.

**Solution:**

The Lewis electron structure for the $NH_4^+$ ion is as follows:



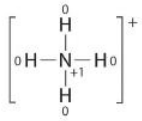
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 4.4.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \tfrac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \tfrac{2}{2}\right) = 0$$

The formal charges on the atoms in the $NH_4^+$ ion are thus

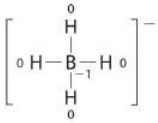


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise

Write the formal charges on all atoms in $BH_4^-$.

**Answer**



If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

### Note the Pattern

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

## Using Formal Charges to Distinguish between Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for $CO_2$. Both structures conform to the rules for Lewis electron structures.

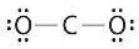
## $CO_2$

1. C is less electronegative than O, so it is the central atom.

2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.

3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.

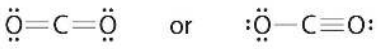
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.

6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of $CO_2$ are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed

experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

### Note the Pattern

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

### Example 5

The thiocyanate ion ($SCN^-$), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

**Given:** chemical species

**Asked for:** Lewis electron structures, formal charges, and preferred arrangement

**Strategy:**

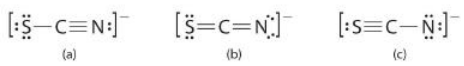
**A** Use the step-by-step procedure to write two plausible Lewis electron structures for $SCN^-$.

**B** Calculate the formal charge on each atom using Equation 4.4.1.

**C** Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

**Solution:**

**A** Possible Lewis structures for the $SCN^-$ ion are as follows:



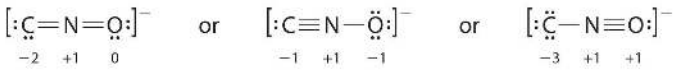

**B** We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6 - \left(6 + \frac{2}{2}\right) = -1.5 - \left(4 + \frac{4}{2}\right) = -1$ In (c), nitrogen has a formal charge of −2.

**C** Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, −1 versus +1, −2.

Exercise

Salts containing the fulminate ion ($CNO^-$) are used in explosive detonators. Draw three Lewis electron structures for $CNO^-$ and use formal charges to predict which is more stable. (Note: N is the central atom.)

**Answer**




The second structure is predicted to be more stable.

## Resonance Structures

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Such is the case for ozone ($O_3$), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

### $O_3$

1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain



and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

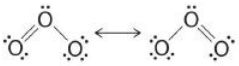


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



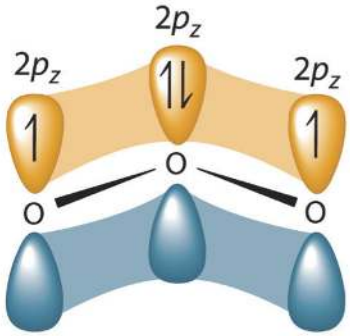

Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn in Section 4.8, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in $O_2$ (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures A Lewis electron structure that has different arrangements of electrons around atoms whose positions do not change.. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



Before the development of quantum chemistry it was thought that the double-headed arrow indicates that the actual electronic structure is an *average* of those shown, or that the molecule oscillates between the two structures. Today we know that the electrons involved in the double bonds occupy an orbital that extends over all three oxygen molecules, combining *p* orbitals on all three.

**Figure 5.3.4 The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms**




*In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered $p_z$ orbitals. Similar molecular orbitals are found in every resonance structure.*

We will discuss the formation of these molecular orbitals in the next chapter but it is important to understand that resonance structures are based on molecular orbitals not averages of different bonds between atoms. We describe the electrons in such molecular orbitals as being delocalized, that is they cannot be assigned to a bond between two atoms.

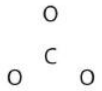
### Note the Pattern

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure involves a molecular orbital which is a linear combination of atomic orbitals from each of the atoms.

## $CO_3^{2-}$

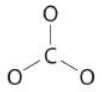
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike $O_3$, though, the Lewis structures describing $CO_3^{2-}$ has *three* equivalent representations.

1. Because carbon is the least electronegative element, we place it in the central position:

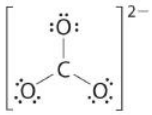


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

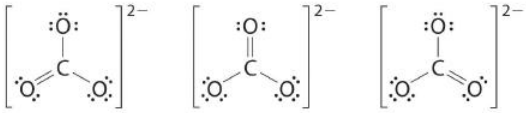


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

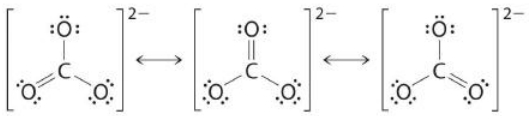


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



As the case for ozone, the actual structure involves the formation of a molecular orbital from $p_z$ orbitals centered on each atom and sitting above and below the plane of the $CO_3^{2-}$ ion.

## Example 6

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule ($C_6H_6$) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

**Given:** molecular formula and molecular geometry

**Asked for:** resonance structures

**Strategy:**

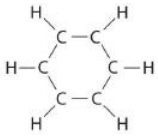
**A** Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

**B** Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

**C** Draw the resonance structures for benzene.

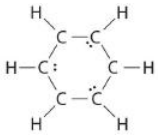
**Solution:**

**A** Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



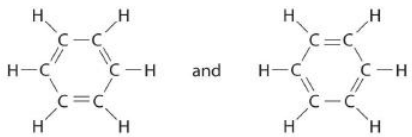
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

**B** If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

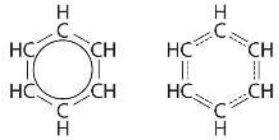


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

**C** There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms.

Exercise

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion ($NO_2^-$).

**Answer**



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

## Summary

A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one. Some molecules have two or more chemically equivalent Lewis electron structures, called **resonance structures**. These structures are written with a double-headed arrow between them, indicating that *none* of the Lewis structures accurately describes the bonding but that the actual structure is an *average* of the individual resonance structures.

## Key Takeaway

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

## Key Equation

**Formal charge on an atom**

Equation 5.3.1: $formal\ charge = valence\ e^- - \left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)$

## Conceptual Problems

1. Compare and contrast covalent and ionic compounds with regard to
    1. volatility.
    2. melting point.
    3. electrical conductivity.
    4. physical appearance.

2. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?
3. Which atom do you expect to be the central atom in each of the following species?
    1. $SO_4^{2-}$
    2. $NH_4^+$
    3. $BCl_3$
    4. $SO_2Cl_2$?
4. Which atom is the central atom in each of the following species?
    1. $PCl_3$
    2. $CHCl_3$
    3. $SO_2$
    4. $IF_3$?
5. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?
6. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?
7. Why are resonance structures important?
8. In what types of compounds are resonance structures particularly common?

## Numerical Problems

1. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
    1. Se
    2. Kr
    3. Li
    4. Sr
    5. H
2. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
    1. Na
    2. Br
    3. Ne
    4. C
    5. Ga
3. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.
4. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.
5. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.
6. Determine the total number of valence electrons in the following.
    1. Cr
    2. $Cu^+$
    3. $NO^+$
    4. $XeF_2$
    5. $Br_2$
    6. $CH_2Cl_2$
    7. $NO_3^-$

8. $H_3O^+$

7. Determine the total number of valence electrons in the following.

    1. Ag
    2. $Pt^{2+}$
    3. $H_2S$
    4. $OH^-$
    5. $I_2$
    6. $CH_4$
    7. $SO_4^{2-}$
    8. $NH_4^+$.

8. Draw Lewis electron structures for the following.

    1. $F_2$
    2. $SO_2$
    3. $AlCl_4^-$
    4. $SO_3^{2-}$
    5. BrCl
    6. $XeF_4$
    7. $NO^+$
    8. $PCl_3$

9. Draw Lewis electron structures for the following.

    1. $Br_2$
    2. $CH_3Br$
    3. $SO_4^{2-}$
    4. $O_2$
    5. $S_2^{2-}$
    6. $BF_3$

10. Draw Lewis electron structures for $CO_2$, $NO_2^-$, $SO_2$, and $NO_2^+$. From your diagram, predict which pair(s) of compounds have similar electronic structures.

11. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

    1. K, S
    2. Sr, Br
    3. Al, O
    4. Mg, Cl

12. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

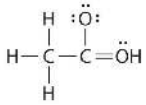
    1. Li, F
    2. Cs, Br
    3. Ca, Cl
    4. B, F

13. Use Lewis dot symbols to predict whether ICl and $NO_4^-$ are chemically reasonable formulas.

14. Draw a plausible Lewis electron structure for a compound with the molecular formula $Cl_3PO$.

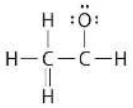
15. Draw a plausible Lewis electron structure for a compound with the molecular formula $CH_4O$.

16. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

17. A student proposed the following Lewis structure shown for acetaldehyde.



Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

18. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.
19. Draw the most plausible Lewis structure for $NO_3^-$. Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.
20. At least two Lewis structures can be drawn for $BCl_3$. Using arguments based on formal charges, explain why the most likely structure is the one with three B–Cl single bonds.
21. Using arguments based on formal charges, explain why the most feasible Lewis structure for $SO_4^{2-}$ has two sulfur–oxygen double bonds.
22. At least two distinct Lewis structures can be drawn for $N_3^-$. Use arguments based on formal charges to explain why the most likely structure contains a nitrogen–nitrogen double bond.
23. Is H–O–N=O a reasonable structure for the compound $HNO_2$? Justify your answer using Lewis electron dot structures.
24. Is H–O=C–H a reasonable structure for a compound with the formula $CH_2O$? Use Lewis electron dot structures to justify your answer.
25. Explain why the following Lewis structure for $SO_3^{2-}$ is or is not reasonable.



26. Draw all the resonance structures for each ion.
    1. $HSO_4^-$
    2. $HSO_3^-$

## Answers

1. 1. $[Ar]4s^23d^{10}4p^4$



   Selenium can accommodate two more electrons, giving the $Se^{2-}$ ion.

   2. $[Ar]4s^23d^{10}4p^6$



   Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

   3. $1s^22s^1$



Lithium can accommodate one additional electron in its 2*s* orbital, giving the $Li^-$ ion.

4. [Kr]$5s^2$



Strontium has a filled 5*s* subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

5. $1s^1$



Hydrogen can accommodate one additional electron in its 1*s* orbital, giving the $H^-$ ion.

2.

3. $Be^{2+}$, $F^-$, $B^{3+}$, $Cs^+$

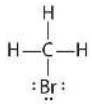
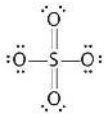
4.

5.

6.

7. 1. 11
   2. 8
   3. 8
   4. 8
   5. 14
   6. 8
   7. 32
   8. 8

8.

9. 1. 
   2. 
   3. 
   4. 
   5. 
   6. 

10.

11. 1. 

    K is the reductant; S is the oxidant. The final stoichiometry is $K_2S$.

    2. 

    Sr is the reductant; Br is the oxidant. The final stoichiometry is $SrBr_2$.

    3. 

    Al is the reductant; O is the oxidant. The final stoichiometry is $Al_2O_3$.

4. 

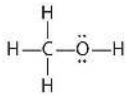
Mg is the reductant; Cl is the oxidant. The final stoichiometry is $MgCl_2$.

12.

13.

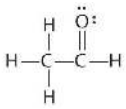
14.

15. The only structure that gives both oxygen and carbon an octet of electrons is the following:

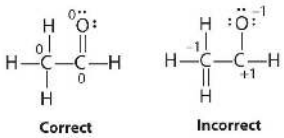


16.

17. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is

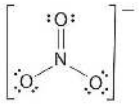


The formal charges on the correct and incorrect structures are as follows:



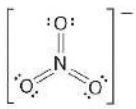

18.

19. The most plausible Lewis structure for $NO_3^-$ is:



There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is −1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



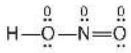
This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of –1.

20.

21. With four S–O single bonds, each oxygen in $SO_4^{2-}$ has a formal charge of −1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of –1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.

22.

23. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an octet of electrons.



24.
25.
26.

## Contributors

- Anonymous

Modified by Joshua Halpern

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# 8.6: Exceptions to the Octet Rule

**Learning Objectives**

- To understand why there are exceptions to the octet rule and what they are

General exceptions to the octet rule include molecules that have an odd number of electrons and molecules in which one or more atoms possess more or fewer than eight electrons. Molecules with an odd number of electrons are relatively rare in the *s* and *p* blocks but rather common among the *d*- and *f*-block elements. Compounds with more than an octet of electrons around an atom are called **expanded-valence molecules**. One model to explain their existence uses one or more *d* orbitals in bonding in addition to the valence *ns* and *np* orbitals. Such species are known for only atoms in period 3 or below, which contain *nd* subshells in their valence shell. Learning Objective is to assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Lewis dot structures provide a simple model for rationalizing the bonding in most known compounds. However, there are three general exceptions to the octet rule:

1. Molecules, such as NO, with an *odd* number of electrons;
2. Molecules in which one or more atoms possess *more* than eight electrons, such as $SF_6$; and
3. Molecules such as $BCl_3$, in which one or more atoms possess *less* than eight electrons.

## Odd Number of Electrons

Because most molecules or ions that consist of *s*- and *p*-block elements contain even numbers of electrons, their bonding can be described using a model that assigns every electron to either a bonding pair or a lone pair. Molecules or ions containing *d*-block elements frequently contain an odd number of electrons, and their bonding cannot adequately be described using the simple approach we have developed so far. There are, however, a few molecules containing only *p*-block elements that have an odd number of electrons. Some important examples are nitric oxide (NO), whose biochemical importance was described in earlier chapters; nitrogen dioxide ($NO_2$), an oxidizing agent in rocket propulsion; and chlorine dioxide ($ClO_2$), which is used in water purification plants. Consider NO, for example. With 5 + 6 = 11 valence electrons, there is no way to draw a Lewis structure that gives each atom an octet of electrons. Molecules such as NO, $NO_2$, and $ClO_2$ require a more sophisticated treatment of bonding.

Example 1: The *NO* Molecule

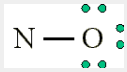
Draw the Lewis structure for the molecule nitrous oxide (NO).

**Solution**

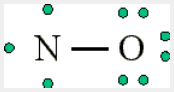
1. Total electrons: 6+5=**11**
2. Bonding structure:




3. Octet on "outer" element:




4. Remainder of electrons (11-8 = 3) on "central" atom:



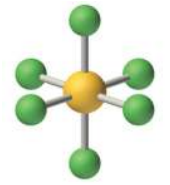

5. There are currently 5 valence electrons around the nitrogen. A double bond would place 7 around the nitrogen, and a triple bond would place 9 around the nitrogen.

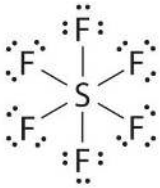
***We appear unable to get an octet around each atom***

## More Than an Octet of Electrons

The most common exception to the octet rule is a molecule or an ion with at least one atom that possesses more than an octet of electrons. Such compounds are found for elements of period 3 and beyond. Examples from the *p*-block elements include $SF_6$, a substance used by the electric power industry to insulate high-voltage lines, and the $SO_4^{2-}$ and $PO_4^{3-}$ ions.

Let's look at sulfur hexafluoride ($SF_6$), whose Lewis structure must accommodate a total of 48 valence electrons [6 + (6 × 7) = 48]. If we arrange the atoms and electrons symmetrically, we obtain a structure with six bonds to sulfur; that is, it is *six-coordinate*. Each fluorine atom has an octet, but the sulfur atom has 12 electrons surrounding it rather than 8.The third step in our procedure for writing Lewis electron structures, in which we place an electron pair between each pair of bonded atoms, requires that an atom have more than 8 electrons whenever it is bonded to more than 4 other atoms.

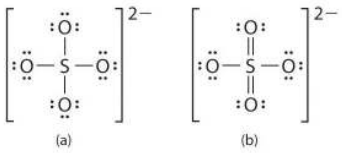

Sulfur hexafluoride



The octet rule is based on the fact that each valence orbital (typically, one *ns* and three *np* orbitals) can accommodate only two electrons. To accommodate more than eight electrons, sulfur must be using not only the *ns* and *np* valence orbitals but additional orbitals as well. Sulfur has an $[Ne]3s^2 3p^4 3d^0$ electron configuration, so in principle it could accommodate more than eight valence electrons by using one or more *d* orbitals. Thus species such as $SF_6$ are often called expanded-valence molecules. Whether or not such compounds really do use *d* orbitals in bonding is controversial, but this model explains why compounds exist with more than an octet of electrons around an atom.

There is no correlation between the stability of a molecule or an ion and whether or not it has an expanded valence shell. Some species with expanded valences, such as $PF_5$, are highly reactive, whereas others, such as $SF_6$, are very unreactive. In fact, $SF_6$ is so inert that it has many commercial applications. In addition to its use as an electrical insulator, it is used as the coolant in some nuclear power plants, and it is the pressurizing gas in "unpressurized" tennis balls.

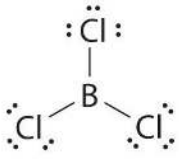
An expanded valence shell is often written for oxoanions of the heavier *p*-block elements, such as sulfate ($SO_4^{2-}$) and phosphate ($PO_4^{3-}$). Sulfate, for example, has a total of 32 valence electrons [6 + (4 × 6) + 2]. If we use a single pair of electrons to connect the sulfur and each oxygen, we obtain the four-coordinate Lewis structure (a). We know that sulfur can accommodate more than eight electrons by using its empty valence *d* orbitals, just as in $SF_6$. An alternative structure (b) can be written with S=O double bonds, making the sulfur again six-coordinate. We can draw five other resonance structures equivalent to (b) that vary only in the arrangement of the single and double bonds. In fact, experimental data show that the S-to-O bonds in the $SO_4^{2-}$ ion are intermediate in length between single and double bonds, as expected for a system whose resonance structures all contain two S–O single bonds and two S=O double bonds. When calculating the formal charges on structures (a) and (b), we see that the S atom in (a) has a formal charge of +2, whereas the S atom in (b) has a formal charge of 0. Thus by using an expanded octet, a +2 formal charge on S can be eliminated.


(a)

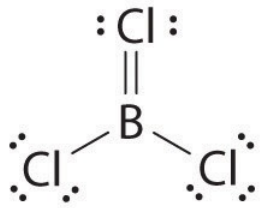

(b)

## Less Than an Octet of Electrons

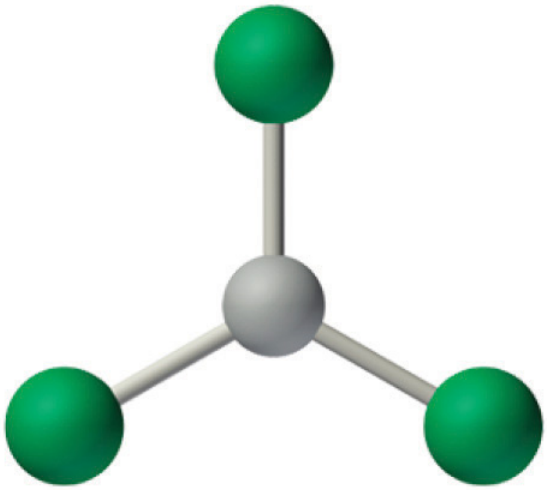
Molecules with atoms that possess less than an octet of electrons generally contain the lighter *s*- and *p*-block elements, especially beryllium, typically with just four electrons around the central atom, and boron, typically with six. One example, boron trichloride ($BCl_3$) is used to produce fibers for reinforcing high-tech tennis rackets and golf clubs. The compound has 24 valence electrons and the following Lewis structure:



The boron atom has only six valence electrons, while each chlorine atom has eight. A reasonable solution might be to use a lone pair from one of the chlorine atoms to form a B-to-Cl double bond:




This resonance structure, however, results in a formal charge of +1 on the doubly bonded Cl atom and −1 on the B atom. The high electronegativity of Cl makes this separation of charge unlikely and suggests that this is not the most important resonance structure for $BCl_3$. This conclusion is shown to be valid based on the three equivalent B–Cl bond lengths of 173 pm that have no double bond character. Electron-deficient compounds such as $BCl_3$ have a strong tendency to gain an additional pair of electrons by reacting with species with a lone pair of electrons.



Boron trichloride

Example 8

Draw Lewis dot structures for each compound.

a. $BeCl_2$ gas, a compound used to produce beryllium, which in turn is used to produce structural materials for missiles and communication satellites

b. $SF_4$, a compound that reacts violently with water

Include resonance structures where appropriate.

**Given:** two compounds

**Asked for:** Lewis electron structures

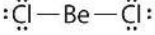
**Strategy:**

A. Use the procedure given earlier to write a Lewis electron structure for each compound. If necessary, place any remaining valence electrons on the element most likely to be able to accommodate more than an octet.

B. After all the valence electrons have been placed, decide whether you have drawn an acceptable Lewis structure.

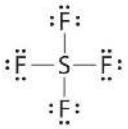
**Solution:**

a. **A** Because it is the least electronegative element, Be is the central atom. The molecule has 16 valence electrons (2 from Be and 7 from each Cl). Drawing two Be–Cl bonds and placing three lone pairs on each Cl gives the following structure:

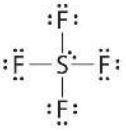


**B** Although this arrangement gives beryllium only 4 electrons, it is an acceptable Lewis structure for $BeCl_2$. Beryllium is known to form compounds in which it is surrounded by less than an octet of electrons.

b. **A** Sulfur is the central atom because it is less electronegative than fluorine. The molecule has 34 valence electrons (6 from S and 7 from each F). The S–F bonds use 8 electrons, and another 24 are placed around the F atoms:



The only place to put the remaining 2 electrons is on the sulfur, giving sulfur 10 valence electrons:

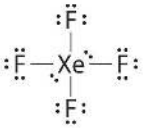


**B** Sulfur can accommodate more than an octet, so this is an acceptable Lewis structure.

Exercise 8

Draw Lewis dot structures for $XeF_4$.

**Answer**



Note

- In oxoanions of the heavier *p*-block elements, the central atom often has an expanded valence shell.
- Molecules with atoms that have fewer than an octet of electrons generally contain the lighter *s*- and *p*-block elements.
- Electron-deficient compounds have a strong tendency to gain electrons in their reactions.

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# 8.7: Lewis Acids and Bases

**Learning Objectives**

- To identify Lewis acids and bases.

A **Lewis acid** is a compound with a strong tendency to *accept* an additional pair of electrons from a **Lewis base**, which can *donate* a pair of electrons. Such an acid–base reaction forms an **adduct**, which is a compound with a *coordinate covalent bond* in which both electrons are provided by only one of the atoms. **Electron-deficient molecules**, which have less than an octet of electrons around one atom, are relatively common. They tend to acquire an octet electron configuration by reacting with an atom having a lone pair of electrons. Learning Objective is to identify Lewis acids and bases.

## Introduction

The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. A Lewis base is defined as any species that can *donate* a pair of electrons, and a Lewis acid is any species that can *accept* a pair of electrons. All Brønsted–Lowry bases (proton acceptors), such as $OH^-$, $H_2O$, and $NH_3$, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the $H^+$ ion.

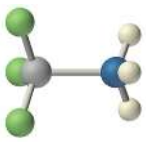
Electron-deficient molecules, such as $BCl_3$, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:

$$\underset{\substack{\text{Lewis acid}\\ \text{Electron-pair}\\ \text{acceptor}}}{H^+} + \underset{\substack{\text{Lewis base}\\ \text{Electron-pair}\\ \text{donor}}}{:B} \longrightarrow H{:}B^+$$

The proton ($H^+$), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride ($BF_3$):

$$\underset{\substack{\text{Lewis}\\ \text{acid}}}{BF_3} + \underset{\substack{\text{Lewis}\\ \text{base}}}{:NH_3} \longrightarrow \underset{\substack{\text{Acid-base}\\ \text{adduct}}}{F_3B{:}NH_3}$$

The bond formed between a Lewis acid and a Lewis base is a *coordinate covalent bond* because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in $H_2O$. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure 8.7.1 for boron trichloride and diethyl ether:

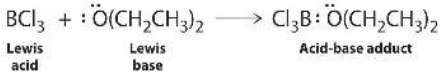
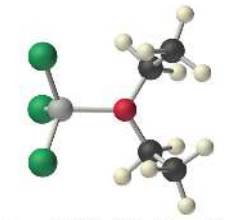



***Figure 8.7.1**: Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction*

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.




A typical example is the reaction of the hydroxide ion with carbon dioxide to give the bicarbonate ion, as shown in Figure 8.7.2. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

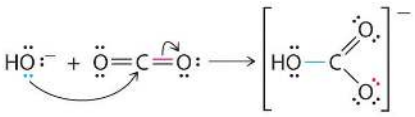



***Figure 8.7.2**: Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide*

## Example 8.7.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

**Given:** reactants and products

**Asked for:** identity of Lewis acid and Lewis base

**Strategy:**

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

**Solution:**

a. In $BH_3$, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of $BH_3$. The Lewis base is $(CH_3)_2S$, and the Lewis acid is $BH_3$.
b. As in the reaction shown in Equation 8.21, $CO_2$ accepts a pair of electrons from the $O^{2-}$ ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so $CO_2$ is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

## Exercise 8.7.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

**Answer**

a. Lewis base: $(CH_3)_2O$; Lewis acid: $BF_3$
b. Lewis base: $H_2O$; Lewis acid: $SO_3$

## Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

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# 8.8: Properties of Covalent Bonds

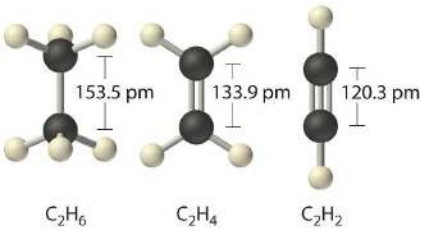
**Learning Objectives**

- To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds.

## Bond Order

When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order The number of electron pairs that hold two atoms together.. For a single bond, such as the C–C bond in $H_3C–CH_3$, the bond order is one. For a double bond (such as $H_2C=CH_2$), the bond order is two. For a triple bond, such as HC≡CH, the bond order is three.




When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table 5.5.1 for example, show that the C–C distance in $H_3C–CH_3$ (153.5 pm) is longer than the distance in $H_2C=CH_2$ (133.9 pm), which in turn is longer than that in HC≡CH (120.3 pm). Additionally, as noted in Section 5.3, molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

**Table 5.5.1 Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K**

| Compound | Bond Order | Bond Length (pm) | Bond Dissociation Energy (kJ/mol) | Compound | Bond Order | Bond Length (pm) | Bond Dissociation Energy (kJ/mol) |
|---|---|---|---|---|---|---|---|
| $H_3C–CH_3$ | 1 | 153.5 | 376 | $H_3C–NH_2$ | 1 | 147.1 | 331 |
| $H_2C=CH_2$ | 2 | 133.9 | 728 | $H_2C=NH$ | 2 | 127.3 | 644 |
| HC≡CH | 3 | 120.3 | 965 | HC≡N | 3 | 115.3 | 937 |
| $H_2N–NH_2$ | 1 | 144.9 | 275.3 | $H_3C–OH$ | 1 | 142.5 | 377 |
| HN=NH | 2 | 125.2 | 456 | $H_2C=O$ | 2 | 120.8 | 732 |
| N≡N | 3 | 109.8 | 945.3 | O=C=O | 2 | 116.0 | 799 |
| HO–OH | 1 | 147.5 | 213 | C≡O | 3 | 112.8 | 1076.5 |
| O=O | 2 | 120.7 | 498.4 | | | | |

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); http://cccbdb.nist.gov.

## The Relationship between Bond Order and Bond Energy

As shown in Table 5.5.1, triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 5.5.2 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

**Table 5.5.2 Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K**

| Single Bonds | | | | | | | | | | Multiple Bonds | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| H–H | 432 | C–C | 346 | N–N | ≈167 | O–O | ≈142 | F–F | 155 | C=C | 602 |
| H–C | 411 | C–Si | 318 | N–O | 201 | O–F | 190 | F–Cl | 249 | C≡C | 835 |
| H–Si | 318 | C–N | 305 | N–F | 283 | O–Cl | 218 | F–Br | 249 | C=N | 615 |
| H–N | 386 | C–O | 358 | N–Cl | 313 | O–Br | 201 | F–I | 278 | C≡N | 887 |
| H–P | ≈322 | C–S | 272 | N–Br | 243 | O–I | 201 | Cl–Cl | 240 | C=O | 749 |
| H–O | 459 | C–F | 485 | P–P | 201 | S–S | 226 | Cl–Br | 216 | C≡O | 1072 |
| H–S | 363 | C–Cl | 327 | | | S–F | 284 | Cl–I | 208 | N=N | 418 |
| H–F | 565 | C–Br | 285 | | | S–Cl | 255 | Br–Br | 190 | N≡N | 942 |
| H–Cl | 428 | C–I | 213 | | | S–Br | 218 | Br–I | 175 | N=O | 607 |
| H–Br | 362 | Si–Si | 222 | | | | | I–I | 149 | O=O | 494 |
| H–I | 295 | Si–O | 452 | | | | | | | S=O | 532 |

*Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).*

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 5.5.1).

2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 5.5.1. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

Cl–Cl > Br–Br > F–F > I–I

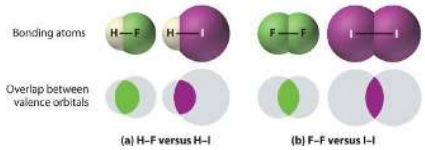
Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

### Note the Pattern

Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

**Figure 5.5.1 The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms**




*The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space relative to the size of the bonded atom decreases; that is, the percentage of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.*

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the $SO_4^{2-}$ ion in Section 5.4. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, $SiO_2$ has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of $SiO_2$ very different from those of $CO_2$.

### Note the Pattern

Bond strengths increase as bond order increases, while bond distances decrease.

## The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 5.5.3 ); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 5.5.3 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

**Table 5.5.3 Energies for the Dissociation of Successive C–H Bonds in Methane**

| Reaction | *D* (kJ/mol) |
|---|---|
| $CH_4(g) \rightarrow CH_3(g) + H(g)$ | 439 |
| $CH_3(g) \rightarrow CH_2(g) + H(g)$ | 462 |
| $CH_2(g) \rightarrow CH(g) + H(g)$ | 424 |
| $CH(g) \rightarrow C(g) + H(g)$ | 338 |

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

### Summary

**Bond order** is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

## Key Takeaway

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

## Conceptual Problems

1. Which would you expect to be stronger—an S–S bond or an Se–Se bond? Why?
2. Which element—nitrogen, phosphorus, or arsenic—will form the strongest multiple bond with oxygen? Why?
3. Why do multiple bonds between oxygen and period 3 elements tend to be unusually strong?
4. What can bond energies tell you about reactivity?
5. Bond energies are typically reported as average values for a range of bonds in a molecule rather than as specific values for a single bond? Why?
6. If the bonds in the products are weaker than those in the reactants, is a reaction exothermic or endothermic? Explain your answer.
7. A student presumed that because heat was required to initiate a particular reaction, the reaction product would be stable. Instead, the product exploded. What information might have allowed the student to predict this outcome?

## Numerical Problems

1. What is the bond order about the central atom(s) of hydrazine ($N_2H_4$), nitrogen, and diimide ($N_2H_2$)? Draw Lewis electron structures for each compound and then arrange these compounds in order of increasing N–N bond distance. Which of these compounds would you expect to have the largest N–N bond energy? Explain your answer.
2. What is the carbon–carbon bond order in ethylene ($C_2H_4$), $BrH_2CCH_2Br$, and FCCH? Arrange the compounds in order of increasing C–C bond distance. Which would you expect to have the largest C–C bond energy? Why?
3. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
    1. P–P, Sb–Sb
    2. Cl–Cl, I–I
    3. O–O, Se–Se
    4. S–S, Cl–Cl
    5. Al–Cl, B–Cl
4. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
    1. Te–Te, S–S
    2. C–H, Ge–H
    3. Si–Si, P–P
    4. Cl–Cl, F–F
    5. Ga–H, Al–H

## Answer

1. $N_2H_4$, bond order 1; $N_2H_2$, bond order 2; $N_2$, bond order 3; N–N bond distance: $N_2 < N_2H_2 < N_2H_4$; Largest bond energy: $N_2$; Highest bond order correlates with strongest and shortest bond.
2. 
3. 
4. 
5. 
6. 
7. 

## Contributors

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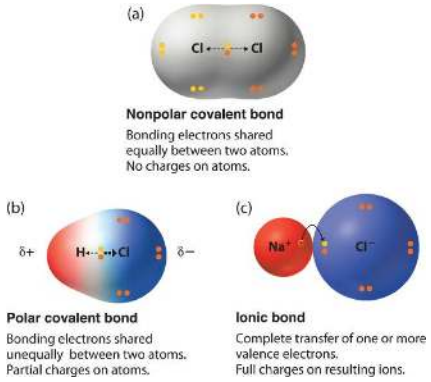
# 8.9: Properties of Polar Covalent Bonds

**Learning Objectives**

- To calculate the percent ionic character of a covalent polar bond.

In Chapter 4, we described the two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds A covalent bond in which the electrons are shared unequally between the bonded atoms., which means that electrons are shared *unequally* between the bonded atoms. Figure 4.7.1 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. A lowercase Greek delta $\delta$ is used to indicate that a bonded atom possesses a partial positive charge, indicated by $\delta^+$ or a partial negative charge, indicated by $\delta^-$ and a bond between two atoms that possess partial charges is a *polar bond*.

**Figure 5.6.1 The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures**




In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

## Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. In Chapter 3, electronegativity ($\chi$) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B ($\chi_B$) is greater than the electronegativity of A ($\chi_A$), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\text{less electronegative}}{A}} - \underset{\delta^-}{\overset{\text{more electronegative}}{B}}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in $Cl_2$, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl}$ = 3.16, $\chi_H$ = 2.20, and $\chi_{Na}$ = 0.93 (see Figure 3.3.2 ). $Cl_2$ must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic

compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form $Na^+$ and $Cl^-$ ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta+}{H} \quad - \quad \overset{\delta-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

### Note the Pattern

Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, $Cl_2$, $ClF_5$, and $HClO_4$ would be exactly the same.

## Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where $Qr$ in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge *Q* on the bonded atoms and the distance *r* between the partial charges:

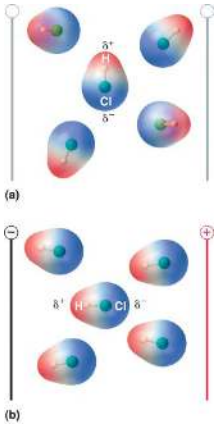
$$\mu = Qr$$

where *Q* is measured in coulombs (C) and *r* in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot \cdot m$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 5.6.2).

**Figure 5.6.2 Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field**




*In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.*

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 5.6.2 If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \tag{5.6.4}$$
$$= 2.901 \times 10^{-20}\ C$$

By dividing this calculated value by the charge on a single electron ($1.6022 \times 10^{-19}$ C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 $e^-$. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} = 0.1811\ e^- \tag{5.6.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as \( \begin{matrix}
_{\delta ^{+}}& & _{\delta ^{-}}\
H\; \; &-& Cl
\end{matrix} \) we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} \quad - \quad \overset{0.18\delta^-}{Cl}$$

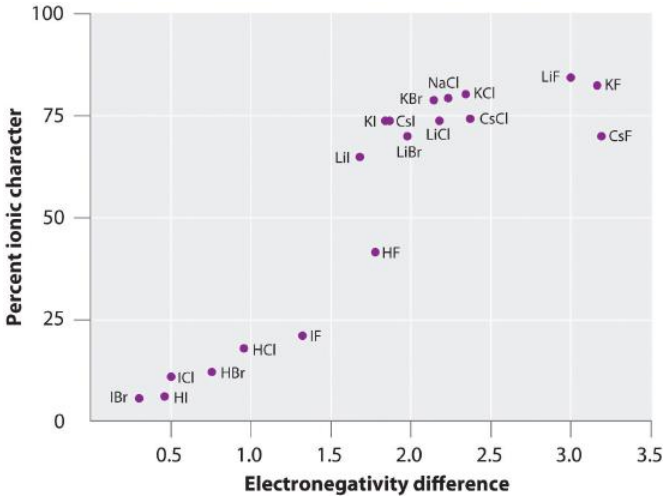
Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:




The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 5.6.3 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 5.6.3 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 9

**Figure 5.6.3 A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms**





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In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

### Example 9

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

**Given:** chemical species, dipole moment, and internuclear distance

**Asked for:** percent ionic character

**Strategy:**

**A** Compute the charge on each atom using the information given

**B** Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

**Solution:**

**A** The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \cancel{D} \left( \frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left( \frac{1}{236.1\ \cancel{pm}} \right) \left( \frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C$$

Thus NaCl behaves as if it had charges of $1.272 \times 10^{-19}$ C on each atom separated by 236.1 pm.

**B** The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left( \frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\%$$

Exercise

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

**Answer:** 55.5%

### Summary

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

### Key Takeaway

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

### Key Equation

**Dipole moment**

Equation 4.7.2 $\mu = Qr$

### Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

### Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.

1. RbCl
2. $S_8$
3. $TiCl_2$
4. $SbCl_3$
5. LiI
6. $Br_2$

2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

    1. NO
    2. HF
    3. MgO
    4. $AlCl_3$
    5. $SiO_2$
    6. the C=O bond in acetone
    7. $O_3$

3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

    1. NaBr
    2. $OF_2$
    3. $BCl_3$
    4. the S–S bond in $CH_3CH_2SSCH_2CH_3$
    5. the C–Cl bond in $CH_2Cl_2$
    6. the O–H bond in $CH_3OH$
    7. $PtCl_4^{2-}$

4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.

    1. CaO
    2. $S_8$
    3. $AlBr_3$
    4. ICl
    5. $Na_2S$
    6. $SiO_2$
    7. LiBr

5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?

6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.

7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.

8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, $r$ = 228.69 pm and μ = 3.59 D; for PbO, $r$ = 192.18 pm and μ = 4.64 D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

## Contributors

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# 8.10: Metallic Bonding

**Learning Objectives**

- To learn about metallic bonding

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure.

- Metals that are malleable can be beaten into thin sheets, for example: aluminum foil.
- Metals that are ductile can be drawn into wires, for example: copper wire.

In the 1900's, Paul Drüde came up with the sea of electrons theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. For example: metallic cations are shown in green surrounded by a "sea" of electrons, shown in purple. This model assumes that the valence electrons do not interact with each other. This model may account for:

- Malleability and Ductility: The sea of electrons surrounding the protons act like a cushion, and so when the metal is hammered on, for instance, the over all composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact.
- Heat capacity: This is explained by the ability of free electrons to move about the solid.
- Luster: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.
- Conductivity: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end, the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

Amazingly, Drude's electron sea model predates Rutherford's nuclear model of the atom and Lewis' octet rule. It is, however, a useful qualitative model of metallic bonding even to this day. As it did for Lewis' octet rule, the quantum revolution of the 1930s told us about the underlying chemistry. Drude's electron sea model assumed that valence electrons were free to move in metals, quantum mechanical calculations told us why this happened.

## Metallic bonding in sodium

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table.

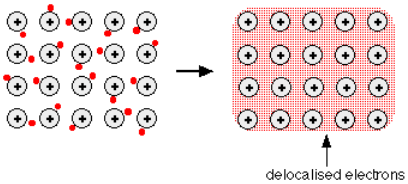
Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium.

All of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals which extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons.

**Figure 5.7.1: Delocaized electrons are free to move in the metallic lattice**




This is sometimes described as "an array of positive ions in a sea of electrons".

Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron hasn't been lost - it may no longer have an attachment to a particular atom, but those electrons are still there in the structure. Sodium metal is therefore written as Na - not $Na^+$.

## Metallic bonding in magnesium

If you work through the same argument with magnesium, you end up with stronger bonds and so a higher melting point.

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalised, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalised electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals.

That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalised electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

## Metallic bonding in transition elements

Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

The strength of a metallic bond depends on three things:

1. The number of electrons that become delocalized from the metal
2. The charge of the cation (metal).
3. The size of the cation.

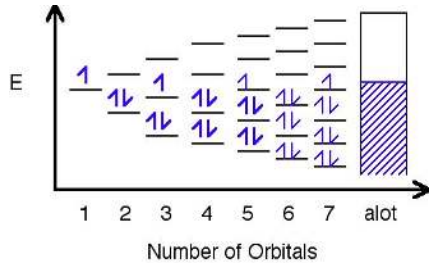
A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.**

A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

## Band Theory

Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch had the idea to take the quantum theory and apply it to solids. In 1927, Walter Heitler and Fritz London explained how these many levels can combine together to form bands- orbitals so close together in energy that they are continuous

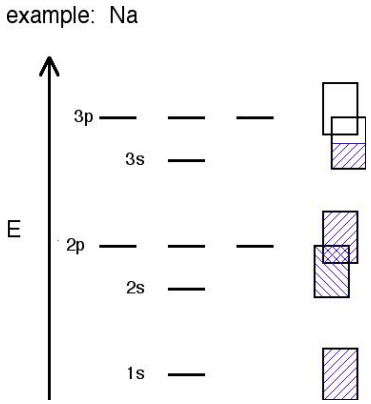
**Figure 5.7.2: Overlap of orbitals from neighboring ions form electron bands**




In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.

**Figure 5.7.3: In different metals different bands are full or available for conduction electrons**




Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

The probability of finding an electron in the conduction band is shown by the equation:

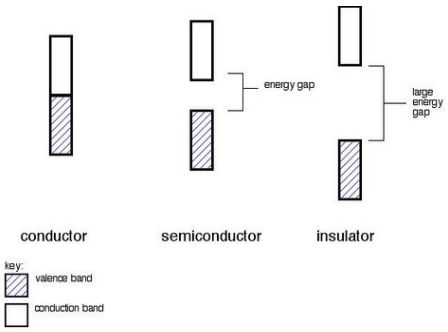
$$P = \frac{1}{e^{\Delta E/RT} + 1}$$

The ΔE in the equation stands for the change in energy or energy gap. t stands for the temperature, and R is a bonding constant. That equation and this table below show how the bigger difference in energy is, or gap, between the valence band and the conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

**Table 5.7.1: Band gaps in three semiconductors**

| ELEMENT | ΔE(kJ/mol) of energy gap | # of electrons/$cm^3$ in conduction band @ 300K | insulator, or conductor? |
|---|---|---|---|
| C (diamond) | 524 (big band gap) | $10^{-27}$ | insulator |
| Si | 117 (smaller band gap, but not a full conductor) | $10^{9}$ | semiconductor |
| Ge | 66 (smaller band gap, but still not a full conductor) | $10^{13}$ | semiconductor |

## Conductors, Insulators and Semiconductors




### A. Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

### B. Insulators

In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

### C. Semiconductors

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

### Outside Links

- http://www.youtube.com/watch?v=HWRHT...87AF6948F5E8F9 (start at 9 minutes)
- http://www.youtube.com/watch?v=qK6DgAM-q7U (start at 13 minutes)
- http://en.Wikipedia.org/wiki/Metallic_bonding
- Metallic Bonding: http://www.youtube.com/watch?v=CGA8sRwqIFg&feature=youtube_gdata

## Problems

1. How do you distinguish between a valence band and a conduction band?
2. Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?
3. What two methods bring conductivity to semiconductors?
4. You are more likely to find electrons in a conduction band if the energy gap is smaller/larger? 5. The property of being able to be drawn into a wire is called...

## Answers

1. The valence band is the highest band with electrons in it, and the conduction band is the highest band with no electrons in it.
2. Larger
3. Electron transport and hole transport
4. Smaller
5. Ductility

## References


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# 8.11: Molecular Representations

**Learning Objectives**

- To review the differences between covalent and ionic bonding.

The atoms in all substances that contain more than one atom are held together by electrostatic interactionsAn interaction between electrically charged particles such as protons and electrons.—interactions between electrically charged particles such as protons and electrons. Electrostatic attractionAn electrostatic interaction between oppositely charged species (positive and negative) that results in a force that causes them to move toward each other. between oppositely charged species (positive and negative) results in a force that causes them to move toward each other, like the attraction between opposite poles of two magnets. In contrast, electrostatic repulsionAn electrostatic interaction between two species that have the same charge (both positive or both negative) that results in a force that causes them to repel each other. between two species with the same charge (either both positive or both negative) results in a force that causes them to repel each other, as do the same poles of two magnets. Atoms form chemical compounds when the attractive electrostatic interactions between them are stronger than the repulsive interactions. Collectively, we refer to the attractive interactions between atoms as chemical bondsAn attractive interaction between atoms that holds them together in compounds..

Chemical bonds are generally divided into two fundamentally different kinds: ionic and covalent. In reality, however, the bonds in most substances are neither purely ionic nor purely covalent, but they are closer to one of these extremes. Although purely ionic and purely covalent bonds represent extreme cases that are seldom encountered in anything but very simple substances, a brief discussion of these two extremes helps us understand why substances that have different kinds of chemical bonds have very different properties. Ionic compoundsA compound consisting of positively charged ions (cations) and negatively charged ions (anions) held together by strong electrostatic forces. consist of positively and negatively charged ions held together by strong electrostatic forces, whereas covalent compoundsA compound that consists of discrete molecules. generally consist of moleculesA group of atoms in which one or more pairs of electrons are shared between bonded atoms., which are groups of atoms in which one or more pairs of electrons are shared between bonded atoms. In a covalent bondThe electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share., the atoms are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share. We begin our review of structures and formulas by describing covalent compounds.

### Note the Pattern

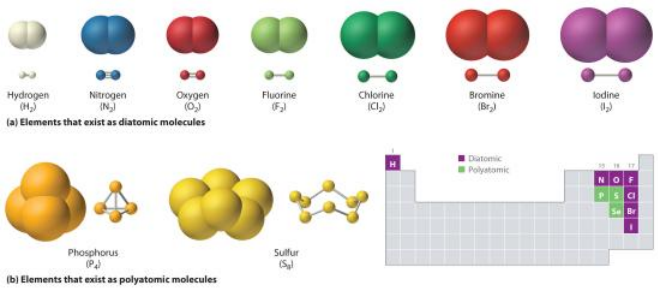
Ionic compounds consist of ions of opposite charges held together by strong electrostatic forces, whereas pairs of electrons are shared between bonded atoms in covalent compounds.

## Covalent Molecules and Compounds

Just as an atom is the simplest unit that has the fundamental chemical properties of an element, a molecule is the simplest unit that has the fundamental chemical properties of a covalent compound. Some pure elements exist as covalent molecules. Hydrogen, nitrogen, oxygen, and the halogens occur naturally as the *diatomic* (“two atoms”) *molecules* $H_2$, $N_2$, $O_2$, $F_2$, $Cl_2$, $Br_2$, and $I_2$ (part (a) in Figure 5.8.1). Similarly, a few pure elements are polyatomicMolecules that contain more than two atoms. (“many atoms”) *molecules*, such as elemental phosphorus and sulfur, which occur as $P_4$ and $S_8$ (part (b) in Figure 5.8.1 ).

Each covalent compound is represented by a molecular formulaA representation of a covalent compound that consists of the atomic symbol for each component element (in a prescribed order) accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number is greater than 1., which gives the atomic symbol for each component element, in a prescribed order, accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number of atoms is greater than 1. For example, water, with two hydrogen atoms and one oxygen atom per molecule, is written as $H_2O$. Similarly, carbon dioxide, which contains one carbon atom and two oxygen atoms in each molecule, is written as $CO_2$.

Figure 5.8.1 Elements That Exist as Covalent Molecules




*(a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula $E_2$. (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as $P_4$ tetrahedra—regular polyhedra with four triangular sides—with a phosphorus atom at each vertex. Elemental sulfur consists of a puckered ring of eight sulfur atoms connected by single bonds. Selenium is not shown due to the complexity of its structure.*

Covalent compounds that contain predominantly carbon and hydrogen are called organic compoundsA covalent compound that contains predominantly carbon and hydrogen.. One convention for representing the formulas of organic compounds is to write carbon first, followed by hydrogen and then any other elements in alphabetical order (e.g., $CH_4O$ is methyl alcohol, a fuel). Another convention better represents the molecular structure as a structural formula, as, for example, writing the formula for methyl alcohol as$CH_3OH$, where $CH_3$ is the methyl group and OH the hydroxyl. Compounds that consist primarily of elements other than carbon and hydrogen are called inorganic compoundsAn ionic or covalent compound that consists primarily of elements other than carbon and hydrogen.; they include both covalent and ionic compounds. In inorganic compounds, the component elements are listed beginning with the one farthest to the left in the periodic table, such as we see in $CO_2$ or $SF_6$. Those in the same group are listed beginning with the lower element and working up, as in ClF. By convention, however, when an inorganic compound contains both hydrogen and an element from groups 13–15, the hydrogen is usually listed last in the formula. Examples are ammonia ($NH_3$) and silane ($SiH_4$). Compounds such as water, whose compositions were established long before this convention was adopted, are always written with hydrogen first: Water is always written as $H_2O$, not $OH_2$. The conventions for inorganic acids, such as hydrochloric acid (HCl) and sulfuric acid ($H_2SO_4$), are described in Section 8.6 .

### Note the Pattern

For organic compounds: write C first, then H, and then the other elements in alphabetical order. For molecular inorganic compounds: start with the element at far left in the periodic table; list elements in same group beginning with the lower element and working up.

### Example 1

Write the molecular formula of each compound.

1. The phosphorus-sulfur compound that is responsible for the ignition of so-called strike anywhere matches has 4 phosphorus atoms and 3 sulfur atoms per molecule.
2. Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
3. Freon-11, once widely used in automobile air conditioners and implicated in damage to the ozone layer, has 1 carbon atom, 3 chlorine atoms, and 1 fluorine atom per molecule.

**Given:** identity of elements present and number of atoms of each

**Asked for:** molecular formula

**Strategy:**

**A** Identify the symbol for each element in the molecule. Then identify the substance as either an organic compound or an inorganic compound.

**B** If the substance is an organic compound, arrange the elements in order beginning with carbon and hydrogen and then list the other elements alphabetically. If it is an inorganic compound, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up.

**C** From the information given, add a subscript for each kind of atom to write the molecular formula.

**Solution:**

1. **A** The molecule has 4 phosphorus atoms and 3 sulfur atoms. Because the compound does not contain mostly carbon and hydrogen, it is inorganic. **B** Phosphorus is in group 15, and sulfur is in group 16. Because phosphorus is to the left of sulfur, it is written first. **C** Writing the number of each kind of atom as a right-hand subscript gives $P_4S_3$ as the molecular formula.
2. **A** Ethyl alcohol contains predominantly carbon and hydrogen, so it is an organic compound. **B** The formula for an organic compound is written with the number of carbon atoms first, the number of hydrogen atoms next, and the other atoms in alphabetical order: CHO. **C** Adding subscripts gives the molecular formula $C_2H_6O$. To convey more structural information we could write this as $C_2H_5OH$. Draw the Lewis structure using this information
3. **A** Freon-11 contains carbon, chlorine, and fluorine. It can be viewed as either an inorganic compound or an organic compound (in which fluorine has replaced hydrogen). The formula for Freon-11 can therefore be written using either of the two conventions.

   **B** According to the convention for inorganic compounds, carbon is written first because it is farther left in the periodic table. Fluorine and chlorine are in the same group, so they are listed beginning with the lower element and working up: CClF. Adding subscripts gives the molecular formula $CCl_3F$.

   **C** We obtain the same formula for Freon-11 using the convention for organic compounds. The number of carbon atoms is written first, followed by the number of hydrogen atoms (zero) and then the other elements in alphabetical order, also giving $CCl_3F$.

Exercise

Write the molecular formula for each compound.

1. Nitrous oxide, also called “laughing gas,” has 2 nitrogen atoms and 1 oxygen atom per molecule. Nitrous oxide is used as a mild anesthetic for minor surgery and as the propellant in cans of whipped cream.
2. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.
3. Sulfur hexafluoride, a gas used to pressurize “unpressurized” tennis balls and as a coolant in nuclear reactors, has 6 fluorine atoms and 1 sulfur atom per molecule.

**Answer**

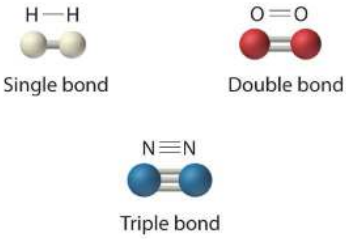
1. $N_2O$
2. $C_{12}H_{22}O_{11}$
3. $SF_6$

## Representations of Molecular Structures

Molecular formulas give only the elemental composition of molecules. In contrast, structural formulasA representation of a molecule that shows which atoms are bonded to one another and, in some cases, the approximate arrangement of atoms in space. show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. These are the Lewis structures we learned about. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

The structural formula for $H_2$ can be drawn as H–H and that for $I_2$ as I–I, where the line indicates a single pair of shared electrons, a single bondA chemical bond formed when two atoms share a single pair of electrons.. Two pairs of electrons are shared in a double bondA chemical bond formed when two atoms share two pairs of electrons., which is indicated by two lines— for example, $O_2$ is O=O. Three electron pairs are shared in a triple bondA chemical bond formed when two atoms share three pairs of electrons., which is indicated by three lines—for example, $N_2$ is N≡N (see Figure 5.8.2). Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is *not* arbitrary. As we have learned in Chapter 4, hydrogen, oxygen, nitrogen, and carbon have a very strong tendency to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Figure 5.8.2).

Figure 5.8.2 Molecules That Contain Single, Double, and Triple Bonds




*Hydrogen ($H_2$) has a single bond between atoms. Oxygen ($O_2$) has a double bond between atoms, indicated by two lines (=). Nitrogen ($N_2$) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron pair.*

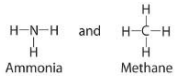
Table 5.8.1 The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

| Atom | Number of Bonds |
|---|---|
| H (group 1) | 1 |
| O (group 16) | 2 |
| N (group 15) | 3 |
| C (group 14) | 4 |

The structural formula for water can be drawn as follows, but including the two lone pairs on the oxygen provides more information:

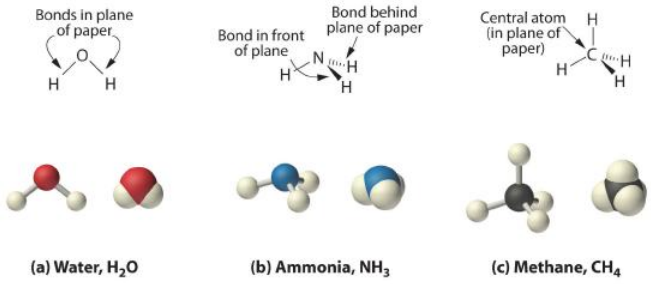


Because as we learned from VSEPR, the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia ($NH_3$) and methane ($CH_4$) are often written as planar molecules but at least for ammonia, it would be more informative to include the lone pair on the nitrogen atom:




As shown in Figure 5.8.3, however, we know that the the actual three-dimensional structure of $NH_3$ looks like a pyramid with a triangular base of three hydrogen atoms. Again using VSEPR, or what we know about sp3 orbitals on the central atom in all three molecules the structure of $CH_4$, with four hydrogen atoms arranged around a central carbon atom as shown in Figure 5.8.3 , is *tetrahedral*. That is, the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.

Figure 5.8.3 The Three-Dimensional Structures of Water, Ammonia, and Methane



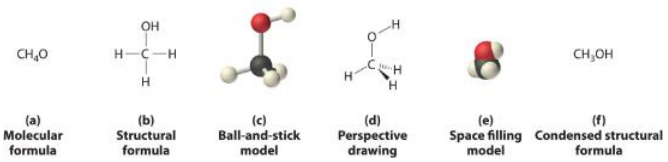

*(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*




***$CH_4$.*** *Methane has a three-dimensional, tetrahedral structure.*

Figure 5.8.1 , and Figure 5.8.3 illustrate different ways to represent the structures of molecules. It should be clear that there is no single "best" way to draw the structure of a molecule; the method you use depends on which aspect of the structure you want to emphasize and how much time and effort you want to spend. Figure 5.8.4 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (part (a) in Figure 5.8.4 ) gives only the number of each kind of atom; writing methanol as $CH_4O$ tells nothing about its structure. In contrast, the structural formula (part (b) in Figure 5.8.4 ) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 5.8.4 ) and the perspective drawing (part (d) in Figure 5.8.4 ) show the three-dimensional structure of the molecule. The latter (also called a *wedge-and-dash* representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 5.8.4 ) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. Also, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

Figure 5.8.4 Different Ways of Representing the Structure of a Molecule




*(a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.*

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a *condensed structural formula* (part (f) in Figure 5.8.4 ), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is $CH_3OH$, which tells us that the molecule contains a $CH_3$ unit that looks like a fragment of methane ($CH_4$). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

## Example 2

Write the molecular formula for each compound. The condensed structural formula is given.

1. Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl.
2. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
3. Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(CH_3)_3N$.

**Given:** condensed structural formula

**Asked for:** molecular formula

**Strategy:**

**A** Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.

**B** As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

**Solution:**

The molecular formula lists the elements in the molecule and the number of atoms of each.

1. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula $S_2Cl_2$.
2. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.
3. **A** The condensed structural formula shows that trimethylamine contains three $CH_3$ units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula $C_3H_9N$.

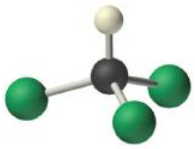


Trimethylamine

Exercise

Write the molecular formula for each molecule.

1. Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms. Its condensed structural formula is $CHCl_3$.
2. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is $H_2NNH_2$.
3. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is $H_2NCH_2CH_2CH_2CH_2NH_2$. This is often written as $H_2N(CH_2)_4NH_2$ to indicate that there are four $CH_2$ fragments linked together.



Chloroform

**Answer**

1. $CHCl_3$
2. $N_2H_4$
3. $C_4H_{12}N_2$

## Ionic Compounds

The substances described in the preceding discussion are composed of molecules that are electrically neutral; that is, the number of positively charged protons in the nucleus is equal to the number of negatively charged electrons. In contrast, *ions* are atoms or assemblies of atoms that have a net electrical charge. Ions that contain fewer electrons than protons have a net positive charge and are called cationsAn ion that has fewer electrons than protons, resulting in a net positive charge.. Conversely, ions that contain more electrons than protons have a net negative charge and are called anionsAn ion that has fewer protons than electrons, resulting in a net negative charge.. *Ionic compounds* contain both cations and anions in a ratio that results in no net electrical charge.

### Note the Pattern

Ionic compounds contain both cations and anions in a ratio that results in zero electrical charge.

In covalent compounds, electrons are shared between bonded atoms and are simultaneously attracted to more than one nucleus. In contrast, ionic compounds contain cations and anions rather than discrete neutral molecules. Ionic compounds are held together by the attractive electrostatic interactions between cations and anions. In an ionic compound, the cations and anions are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 5.8.5 ). As shown in Equation 5.8.1, the electrostatic energy of the interaction between two charged particles is proportional to the product of the charges on the particles and inversely proportional to the distance between them:

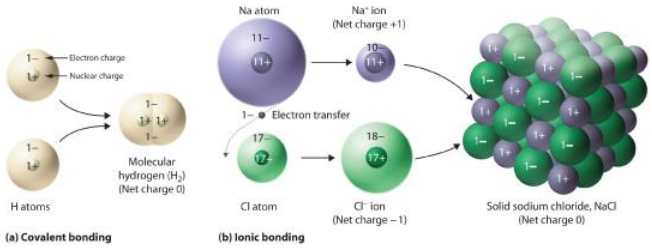
$$electrostatic\ energy = \frac{Q_1 Q_2}{r}$$

where $Q_1$ and $Q_2$ are the electrical charges on particles 1 and 2, and $r$ is the distance between them. When $Q_1$ and $Q_2$ are both positive, corresponding to the charges on cations, the cations repel each other and the electrostatic energy is positive. When $Q_1$ and $Q_2$ are both negative, corresponding to the charges on anions, the anions repel each other and the electrostatic energy is again positive. The electrostatic energy is negative only when the charges have opposite signs; that is, positively charged species are attracted to negatively charged species and vice versa. As shown in Figure 5.8.6 , the strength of the interaction is proportional to the *magnitude* of the charges and decreases as the *distance* between the particles increases as we have seen previously

### Note the Pattern

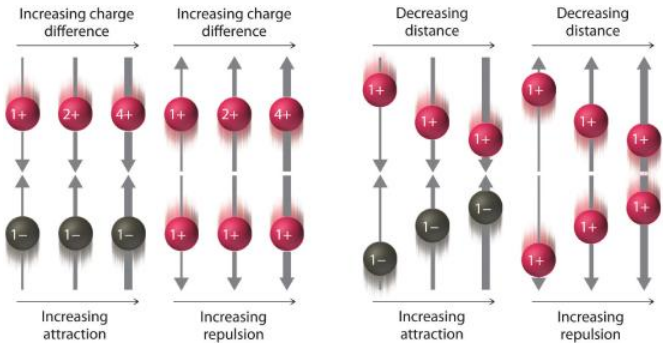
If the electrostatic energy is positive, the particles repel each other; if the electrostatic energy is negative, the particles are attracted to each other.

Figure 5.8.5 Covalent and Ionic Bonding




*(a) In molecular hydrogen ($H_2$), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting $Na^+$ and $Cl^-$ ions form a three-dimensional solid that is held together by attractive electrostatic interactions.*

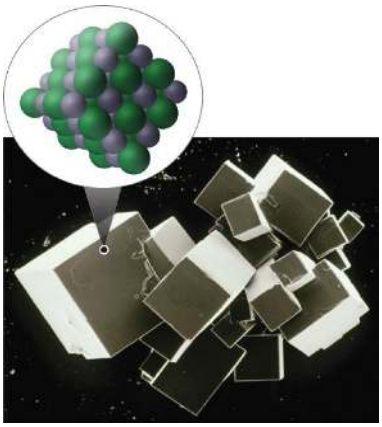
Figure 5.8.6 The Effect of Charge and Distance on the Strength of Electrostatic Interactions




*As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (−…+) or repulsive (−…− or +…+) interactions. The strength of these interactions is represented by the thickness of the arrows.*

One example we have studied of an ionic compound is sodium chloride (NaCl; Figure 5.8.7 ), formed from sodium and chlorine. In forming chemical compounds, many elements have a tendency to gain or lose enough electrons to attain the same number of electrons as the noble gas closest to them in the periodic table. When sodium and chlorine come into contact, each sodium atom gives up an electron to become a $Na^+$ ion, with 11 protons in its nucleus but only 10 electrons (like neon), and each chlorine atom gains an electron to become a $Cl^−$ ion, with 17 protons in its nucleus and 18 electrons (like argon), as shown in part (b) in Figure 5.8.5 . Solid sodium chloride contains equal numbers of cations ($Na^+$) and anions ($Cl^−$), thus maintaining electrical neutrality. Each $Na^+$ ion is surrounded by 6 $Cl^−$ ions, and each $Cl^−$ ion is surrounded by 6 $Na^+$ ions. Because of the large number of attractive $Na^+Cl^−$ interactions, the total attractive electrostatic energy in NaCl is great.

Figure 5.8.7 Sodium Chloride: an Ionic Solid



*The planes of an NaCl crystal reflect the regular three-dimensional arrangement of its $Na^+$ (purple) and $Cl^−$ (green) ions.*

Consistent with a tendency to have the same number of electrons as the nearest noble gas, when forming ions, elements in groups 1, 2, and 3 tend to *lose* one, two, and three electrons, respectively, to form cations, such as $Na^+$ and $Mg^{2+}$. They then have the same number of electrons as the nearest noble gas: neon. Similarly, $K^+$, $Ca^{2+}$, and $Sc^{3+}$ have 18 electrons each, like the nearest noble gas: argon. In addition, the elements in group 13 *lose* three electrons to form cations, such as $Al^{3+}$, again attaining the same number of electrons as the noble gas closest to them in the periodic table. Because the lanthanides and actinides formally belong to group 3, the most common ion formed by these elements is $M^{3+}$, where M represents the metal. Conversely, elements in groups 17, 16, and 15 often react to *gain* one, two, and three electrons, respectively, to form ions such as $Cl^−$, $S^{2−}$, and $P^{3−}$. Ions such as these, which contain only a single atom, are called monatomic ionsAn ion with only a single atom.. The names of the single atom cations are simply the name of the metal from which they are derived. The names of the single atom anions add the suffix -ide to the first syllable of the atom, for example oxide, chloride, nitride, etc.

You can predict the charges of most monatomic ions derived from the main group elements by simply looking at the periodic table and counting how many columns an element lies from the extreme left or right. For example, you can predict that barium (in group 2) will form $Ba^{2+}$ to have the same number of electrons as its nearest noble gas, xenon, that oxygen (in group 16) will form $O^{2−}$ to

have the same number of electrons as neon, and cesium (in group 1) will form $Cs^+$ to also have the same number of electrons as xenon. This method does not usually work for most of the transition metals. Some common monatomic ions are in Table 5.8.2 .

### Note the Pattern

Elements in groups 1, 2, and 3 tend to form 1+, 2+, and 3+ ions, respectively; elements in groups 15, 16, and 17 tend to form 3−, 2−, and 1− ions, respectively.

Table 5.8.2 Some Common Monatomic Ions and Their Names

| Group 1 | Group 2 | Group 3 | Group 13 | Group 15 | Group 16 | Group 17 |
|---|---|---|---|---|---|---|
| $Li^+$ lithium | $Be^{2+}$ beryllium | | | $N^{3-}$ nitride (azide) | $O^{2-}$ oxide | $F^-$ fluoride |
| $Na^+$ sodium | $Mg^{2+}$ magnesium | | $Al^{3+}$ aluminum | $P^{3-}$ phosphide | $S^{2-}$ sulfide | $Cl^-$ chloride |
| $K^+$ potassium | $Ca^{2+}$ calcium | $Sc^{3+}$ scandium | $Ga^{3+}$ gallium | $As^{3-}$ arsenide | $Se^{2-}$ selenide | $Br^-$ bromide |
| $Rb^+$ rubidium | $Sr^{2+}$ strontium | $Y^{3+}$ yttrium | $In^{3+}$ indium | | $Te^{2-}$ telluride | $I^-$ iodide |
| $Cs^+$ cesium | $Ba^{2+}$ barium | $La^{3+}$ lanthanum | | | | |

### Example 3

Predict the charge on the most common monatomic ion formed by each element.

1. aluminum, used in the quantum logic clock, the world's most precise clock
2. selenium, used to make ruby-colored glass
3. yttrium, used to make high-performance spark plugs

**Given:** element

**Asked for:** ionic charge

**Strategy:**

**A** Identify the group in the periodic table to which the element belongs. Based on its location in the periodic table, decide whether the element is a metal, which tends to lose electrons; a nonmetal, which tends to gain electrons; or a semimetal, which can do either.

**B** After locating the noble gas that is closest to the element, determine the number of electrons the element must gain or lose to have the same number of electrons as the nearest noble gas.

**Solution:**

1. **A** Aluminum is a metal in group 13; consequently, it will tend to lose electrons. **B** The nearest noble gas to aluminum is neon. Aluminum will lose three electrons to form the $Al^{3+}$ ion, which has the same number of electrons as neon.
2. **A** Selenium is a nonmetal in group 16, so it will tend to gain electrons. **B** The nearest noble gas is krypton, so we predict that selenium will gain two electrons to form the $Se^{2-}$ ion, which has the same number of electrons as krypton.
3. **A** Yttrium is in group 3, and elements in this group are metals that tend to lose electrons. **B** The nearest noble gas to yttrium is krypton, so yttrium is predicted to lose three electrons to form $Y^{3+}$, which has the same number of electrons as krypton.

Exercise

Predict the charge on the most common monatomic ion formed by each element.

1. calcium, used to prevent osteoporosis

2. iodine, required for the synthesis of thyroid hormones
3. zirconium, widely used in nuclear reactors

**Answer**

1. $Ca^{2+}$
2. $I^-$
3. $Zr^{4+}$

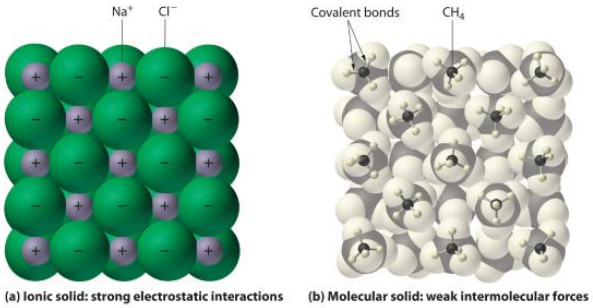
## Physical Properties of Ionic and Covalent Compounds

In general, ionic and covalent compounds have different physical properties. As we have discussed, ionic compounds usually form hard crystalline solids that melt at rather high temperatures and are *very* resistant to evaporation. These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in part (a) in Figure 5.8.8 , which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions. In contrast, as shown in part (b) in Figure 5.8.8 , most covalent compounds consist of discrete molecules held together by comparatively weak *intermolecular* forces (the forces between molecules), even though the atoms within each molecule are held together by strong *intramolecular* covalent bonds (the forces within the molecule). Covalent substances can be gases, liquids, or solids at room temperature and pressure, depending on the strength of the intermolecular interactions. Covalent molecular solids tend to form soft crystals that melt at rather low temperatures and evaporate relatively easily.Some covalent substances, however, are not molecular but consist of infinite three-dimensional arrays of covalently bonded atoms and include some of the hardest materials known, such as diamond. This topic will be addressed in the second semester. The covalent bonds that hold the atoms together in the molecules are unaffected when covalent substances melt or evaporate, so a liquid or vapor of discrete, independent molecules is formed. For example, at room temperature, methane, the major constituent of natural gas, is a gas that is composed of discrete $CH_4$ molecules. A comparison of the different physical properties of ionic compounds and covalent molecular substances is given in Table 5.8.3.

Table 5.8.3 The Physical Properties of Typical Ionic Compounds and Covalent Molecular Substances

| Ionic Compounds | Covalent Molecular Substances |
|---|---|
| hard solids | gases, liquids, or soft solids |
| high melting points | low melting points |
| nonvolatile | volatile |

Figure 5.8.8 Interactions in Ionic and Covalent Solids




(a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane ($CH_4$) molecules in solid methane, a prototypical molecular solid, the methane molecules are held together in the solid only by relatively weak intermolecular forces, even though the atoms within each methane molecule are held together by strong covalent bonds.

### Summary

The atoms in chemical compounds are held together by attractive electrostatic interactions known as **chemical bonds**. **Ionic compounds** contain positively and negatively charged ions in a ratio that results in an overall charge of zero. The ions are held

together in a regular spatial arrangement by electrostatic forces. Most **covalent compounds** consist of **molecules**, groups of atoms in which one or more pairs of electrons are shared by at least two atoms to form a covalent bond. The atoms in molecules are held together by the **electrostatic attraction** between the positively charged nuclei of the bonded atoms and the negatively charged electrons shared by the nuclei. The **molecular formula** of a covalent compound gives the types and numbers of atoms present. Compounds that contain predominantly carbon and hydrogen are called **organic compounds**, whereas compounds that consist primarily of elements other than carbon and hydrogen are **inorganic compounds**. *Diatomic molecules* contain two atoms, and *polyatomic molecules* contain more than two. A **structural formula** indicates the composition and approximate structure and shape of a molecule. **Single bonds, double bonds**, and **triple bonds** are covalent bonds in which one, two, and three pairs of electrons, respectively, are shared between two bonded atoms. Atoms or groups of atoms that possess a net electrical charge are called *ions*; they can have either a positive charge (**cations**) or a negative charge (**anions**). Ions can consist of one atom (**monatomic ions**) or several (*polyatomic ions*). The charges on monatomic ions of most main group elements can be predicted from the location of the element in the periodic table. Ionic compounds usually form hard crystalline solids with high melting points. Covalent molecular compounds, in contrast, consist of discrete molecules held together by weak intermolecular forces and can be gases, liquids, or solids at room temperature and pressure.

### Key Takeaway

- There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties.

### Conceptual Problems

1. Ionic and covalent compounds are held together by electrostatic attractions between oppositely charged particles. Describe the differences in the nature of the attractions in ionic and covalent compounds. Which class of compounds contains pairs of electrons shared between bonded atoms?
2. Which contains fewer electrons than the neutral atom—the corresponding cation or the anion?
3. What is the difference between an organic compound and an inorganic compound?
4. What is the advantage of writing a structural formula as a condensed formula?
5. The majority of elements that exist as diatomic molecules are found in one group of the periodic table. Identify the group.
6. Discuss the differences between covalent and ionic compounds with regard to
    1. the forces that hold the atoms together.
    2. melting points.
    3. physical states at room temperature and pressure.
7. Why do covalent compounds generally tend to have lower melting points than ionic compounds?

### Answer

1. 
2. 
3. 
4. 
5. 
6. 
7. Covalent compounds generally melt at lower temperatures than ionic compounds because the intermolecular interactions that hold the molecules together in a molecular solid are weaker than the electrostatic attractions that hold oppositely charged ions together in an ionic solid.

### Numerical Problems

1. The structural formula for chloroform ($CHCl_3$) was shown in Example 2. Based on this information, draw the structural formula of dichloromethane ($CH_2Cl_2$).

2. What is the total number of electrons present in each ion?

    1. $F^-$
    2. $Rb^+$
    3. $Ce^{3+}$
    4. $Zr^{4+}$
    5. $Zn^{2+}$
    6. $Kr^{2+}$
    7. $B^{3+}$

3. What is the total number of electrons present in each ion?

    1. $Ca^{2+}$
    2. $Se^{2-}$
    3. $In^{3+}$
    4. $Sr^{2+}$
    5. $As^{3+}$
    6. $N^{3-}$
    7. $Tl^+$

4. Predict how many electrons are in each ion.

    1. an oxygen ion with a −2 charge
    2. a beryllium ion with a +2 charge
    3. a silver ion with a +1 charge
    4. a selenium ion with a +4 charge
    5. an iron ion with a +2 charge
    6. a chlorine ion with a −1 charge

5. Predict how many electrons are in each ion.

    1. a copper ion with a +2 charge
    2. a molybdenum ion with a +4 charge
    3. an iodine ion with a −1 charge
    4. a gallium ion with a +3 charge
    5. an ytterbium ion with a +3 charge
    6. a scandium ion with a +3 charge

6. Predict the charge on the most common monatomic ion formed by each element.

    1. chlorine
    2. phosphorus
    3. scandium
    4. magnesium
    5. arsenic
    6. oxygen

7. Predict the charge on the most common monatomic ion formed by each element.

    1. sodium
    2. selenium
    3. barium
    4. rubidium
    5. nitrogen
    6. aluminum

8. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
    1. ${}^{9}_{4}\mathrm{X}_{2+}$
    2. ${}^{1}_{1}\mathrm{X}_{-}$
    3. ${}^{16}_{8}\mathrm{X}_{2-}$
9. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
    1. ${}^{7}_{3}\mathrm{X}_{+}$
    2. ${}^{19}_{9}\mathrm{X}_{-}$
    3. ${}^{27}_{13}\mathrm{X}_{3+}$

## Answers

1.
2.
3.
4.
5. 1. 27
    2. 38
    3. 54
    4. 28
    5. 67
    6. 18
6.
7.
8.
9. 1. Li, $\mathrm{Li}^{+}$, 2nd period, group 1
    2. F, $\mathrm{F}^{-}$, 2nd period, group 17
    3. Al, $\mathrm{Al}^{3+}$, 3nd period, group 13

## Contributors

- Anonymous

Modified by Joshua Halpern

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# CHAPTER OVERVIEW

## 9: Molecular Geometry and Covalent Bonding Models


9.1: Molecular Geometry

9.2: VSEPR - Molecular Geometry

9.3: Hybrid Orbitals

9.4: Delocalized Bonding and Molecular Orbitals

9.5: Polyatomic Systems, Multiple Bonds, Resonance


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# 9.1: Molecular Geometry

**Learning Objectives**

- To extend our models of molecular bonding to determining the shape of molecules.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

Moreover, the exceptions to the Leiws octet model are intellectually troublesome as they are *ad hoc* band aids applied to cases where the simple model does not work. We extend our discussion of structure and bonding to determining the shapes of molecules and orbitals that involve more that two atoms.

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# 9.2: VSEPR - Molecular Geometry

**Learning Objectives**

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

We continue our discussion of structure and bonding by introducing the valence-shell electron-pair repulsion (VSEPR) model A model used to predict the shapes of many molecules and polyatomic ions, based on the idea that the lowest-energy arrangement for a compound is the one in which its electron pairs (bonding and nonbonding) are as far apart as possible. (pronounced “vesper”), which is simple to use to predict the shapes of many molecules and polyatomic ions.

Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds. Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that $H_2S$ and $PH_3$ should have structures similar to those of $H_2O$ and $NH_3$, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in $H_2O$ and $NH_3$. In this section we will make the connection between hybrid orbital described in Chapter 6.2 and VSEPR. The hybrid orbital picture, although more complex, provides a better explanation of such things

More disturbing, the VSEPR model predicts that the simple group 2 halides ($MX_2$), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including $SrF_2$ and $BaF_2$, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. Following sections of this will connect the VSEPR model to molecular orbitals,.

## The VSEPR Model

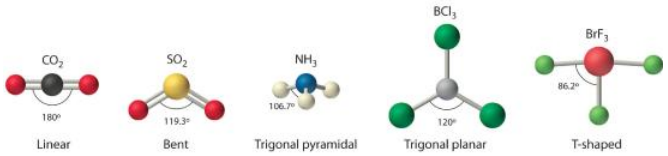
The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is *not* a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

## Note the Pattern

Lewis electron structures predict the number and types of bonds, whereas VSEPR can predict the shapes of many molecules and polyatomic ions.

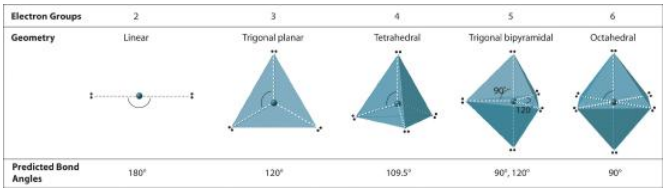
We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 6.3.1 and Figure 6.3.2

**Figure 6.3.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms**




*The VSEPR model explains these differences in molecular geometry.*

**Figure 6.3.2 Geometries for Species with Two to Six Electron Groups**



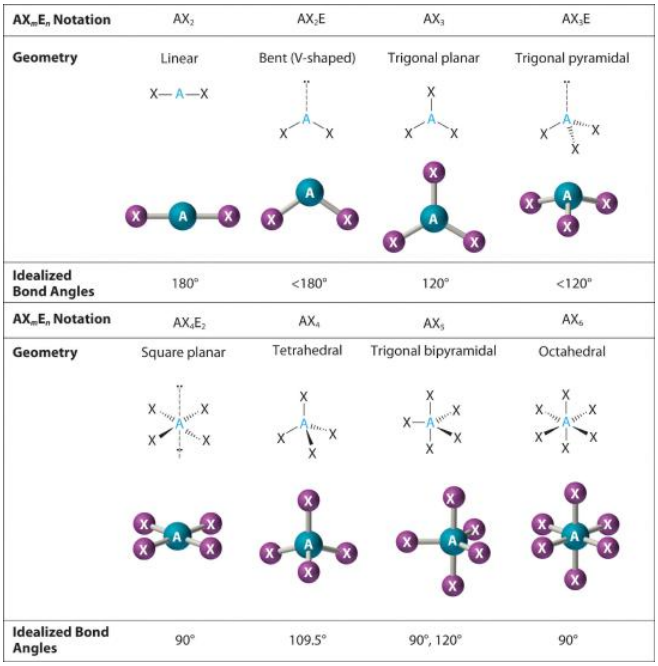

*Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.*

In the VSEPR model, the molecule or polyatomic ion is given an $AX_mE_n$ designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles The angle between bonds.. Using this information, we can describe the molecular geometry The arrangement of the bonded atoms in a molecule or a polyatomic ion in space., the arrangement of the *bonded atoms* in a molecule or polyatomic ion. This procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an $AX_mE_n$ designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 5.1.2 and Figure 5.1.3 , which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

**Figure 6.3.3 Common Molecular Geometries for Species with Two to Six Electron Groups***

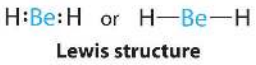



## Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, $BeH_2$.

## $AX_2$: $BeH_2$

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Lewis structure

In this case Be and H each see two electrons which, for those atoms fills the $1s^2$orbitals. This, of course, is an exception to the octet rule, but easy to understand using the aufbau principle

2. There are two electron groups around the central atom. We see from Figure 5.1.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus $BeH_2$ is designated as $AX_2$.

4. From Figure 6.3.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in $BeH_2$ is *linear*.

5. In Section 6.2 we showed that the atomic orbitals of the Be atom were hybridized to for *sp* bonds, which gave $BeH_2$ its linear shape

## $AX_2$: $CO_2$

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is




2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like $BeH_2$, the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so $CO_2$ is designated as $AX_2$.

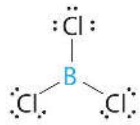
4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of $CO_2$ is linear (Figure 6.3.3 ). The structure of $CO_2$ is shown in Figure 6.3.1

5. If someone asked what the hybridization on the C atom was, we would first draw the Lewis structure. We could then apply VSEPR to the Lewis structure to deduce that the molecular shape of $CO_2$ was linar and from this we conclude that the hybridization of the C atom is *sp*.

# Three Electron Groups

## $AX_3$: $BCl_3$

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

Again, we recognize this as an exception to the octet rule, but again, easy to understand based on what we have studied. The three electrons on the boron atom are shared, one each with each chlorine atom. The chlorine atoms each have a complete octet.

2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 6.3.2 ).

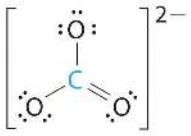
3. All electron groups are bonding pairs (BP), so the structure is designated as $AX_3$.

4. From Figure 6.3.3 we see that with three bonding pairs around the central atom, the molecular geometry of $BCl_3$ is *trigonal planar*, as shown in Figure 6.3.1

5. As discussed in Chapter 6.2, the hybridization on the B atom is $sp^2$ and the shape of the orbitals is triangonal planar.

## $AX_3$: $CO_3^{2-}$

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned in Chapter 4 ", the Lewis electron structure of one of three resonance forms is represented as



**Lewis structure**

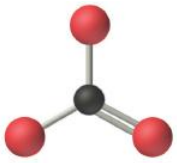
We have already discussed how the electrons in the double bond are smeared over the top and bottom of the ion in a molecular bond and that the bonds linking the carbon and oxygen atoms are identical

2. The structure of $CO_3^{2-}$ is a resonance hybrid. It has three identical bonds, each with a bond order of 1 1/3. We minimize repulsions by placing the three groups 120° apart (Figure 6.3.2 ).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as $AX_3$.

4. We see from Figure 6.3.3 that the molecular geometry of $CO_3^{2-}$ is trigonal planar.

5. Again, the hybridization of the C orbitals is $sp^2$ but there is also a delocalized π orbital above and below the plane.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

## $AX_2E$: $SO_2$

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



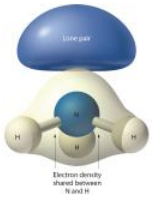
2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 6.3.2 ).

3. There are two bonding pairs and one lone pair, so the structure is designated as $AX_2E$. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 6.3.4 ). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In $SO_2$, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figure 6.3.1 and Figure6.3.3 ).

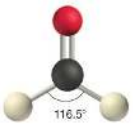
5, Again the hybridization on the central atom (S) is $sp^2$.

**Figure 6.3.4 The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair**



*As with $SO_2$, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.*

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as $CH_2O$ ($AX_3$), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).




## Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

### $AX_4$: $CH_4$

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

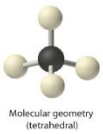


**Lewis structure**

2. There are four electron groups around the central atom. As shown in Figure 6.3.2 repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as $AX_4$.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 6.3.3 ).

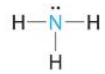



***$CH_4$.*** *Methane has a three-dimensional, tetrahedral structure.*

5. The hybridization of the C atom orbitals is $sp^3$.

### $AX_3E$: $NH_3$

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

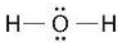
3. With three bonding pairs and one lone pair, the structure is designated as $AX_3E$. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 6.3.3 ). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 6.3.3 and Figure 6.3.4 ).

5. The hybridization of the N atom orbitals is $sp^3$.

## $AX_2E_2$: $H_2O$

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

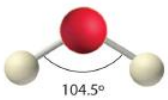


2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 6.3.2

3. With two bonding pairs and two lone pairs, the structure is designated as $AX_2E_2$ with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in $NH_3$, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.

5. The hybridization of the O atom orbitals is $sp^3$.

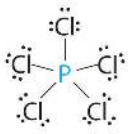



## Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

## $AX_5$: $PCl_5$

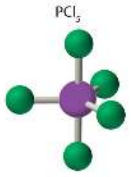
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of $PCl_5$ involves an expanded octet. In the following section we will describe how this expanded octet is formed by the combination of a d orbital with an s and three p orbitals.



2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 6.3.2 ):

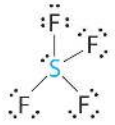
3. All electron groups are bonding pairs, so the structure is designated as $AX_5$. There are no lone pair interactions.

4. The molecular geometry of $PCl_5$ is *trigonal bipyramidal*, as shown in Figure 6.3.3 . The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.




## $AX_4E$: $SF_4$

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



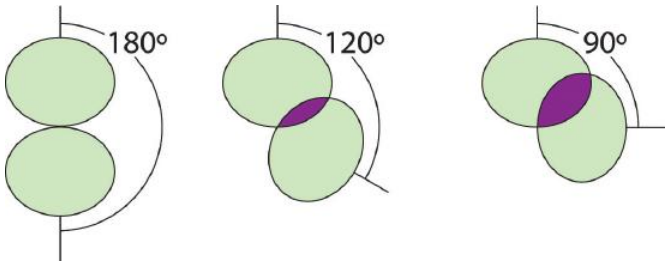

**Lewis structure**

With an expanded valence, this species is an exception to the octet rule and the hybridization of orbitals on the S atom is $sp^3d$..

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 6.3.5

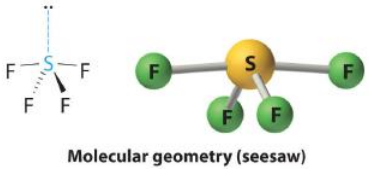
3. We designate $SF_4$ as $AX_4E$; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

**Figure 6.3.5 Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them**




*At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.*

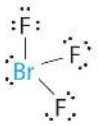
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The $F_{axial}$–S–$F_{axial}$ angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.




**Molecular geometry (seesaw)**

## $AX_3E_2$: $BrF_3$

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



**Lewis structure**

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs and the hybridization of orbitals on the Br atom will be $sp^3d$. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is $AX_3E_2$ with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



| | Lone pairs axial (a) | Lone pairs equatorial (b) | Lone pairs axial and equatorial (c) |
|---|---|---|---|
| **Interactions** | | | |
| 90° LP–LP | 0 | 0 | 1 |
| 90° LP–BP | 6 | 4 | 3 |

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in $BrF_3$ determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The $F_{axial}$–Br–$F_{axial}$ angle is 172°, less than 180° because of LP–BP repulsions (Figure 5.1.1 ).

## Note the Pattern

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

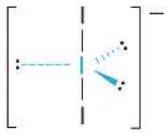
## $AX_2E_3$: $I_3^-$

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



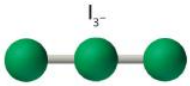
2. There are five electron groups about the central atom in $I_3^-$, two bonding pairs and three lone pairs. The hybridiztion of the orbitals on the central I atom is $sp^3d$. To minimize repulsions, the lone pairs are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, $I_3^-$ has a total of five electron pairs and is designated as $AX_2E_3$. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of $I_3^-$ is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

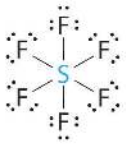



## Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 5.1.2 ).

## $AX_6$: $SF_6$

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



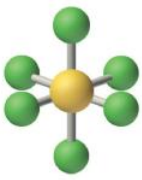

**Lewis structure**

With an expanded valence, we know from Chapter 4 Section 4.6 that this species is an exception to the octet rule and we know that the hybridization of atomic orbitals on the S atom is $sp^3d^2$

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 6.3.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, $SF_6$ is designated as $AX_6$. All positions are chemically equivalent, so all electronic interactions are equivalent.

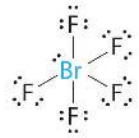
4. There are six nuclei, so the molecular geometry of $SF_6$ is octahedral.



Molecular geometry
(octahedral)

## $AX_5E$: $BrF_5$

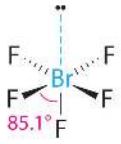
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



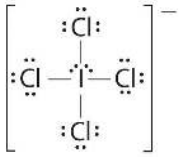

3. With five bonding pairs and one lone pair, $BrF_5$ is designated as $AX_5E$; it has a total of six electron pairs. The $BrF_5$ structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all $F_{axial}$–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The $F_{axial}$–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.

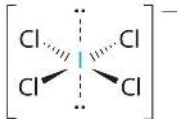

Molecular geometry
(square pyramidal)

## $AX_4E_2$: $ICl_4^-$

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

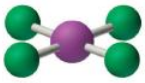



2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is




3. $ICl_4^-$ is designated as $AX_4E_2$ and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the $ICl_4^-$ ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



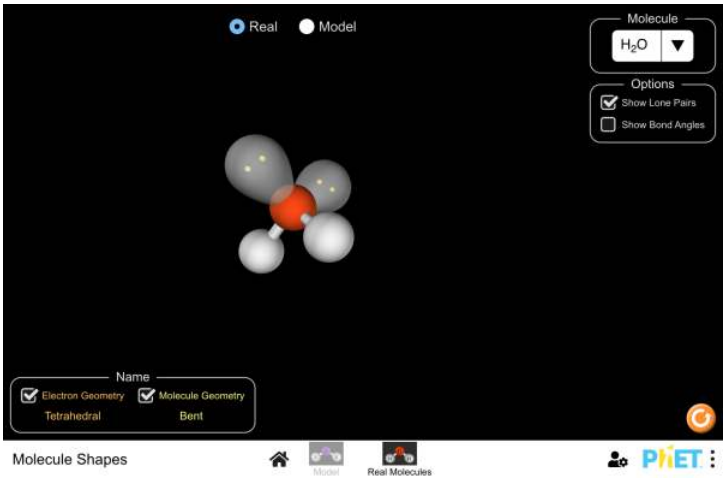
If you would like to try building some of these atoms, here is a PHET applet to play with

The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 6.3.6 .

**Figure 6.3.6 Overview of Molecular Geometries** (Click to make full screen)

| Electron Groups | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| Molecular Geometry | Linear | Trigonal planar | Tetrahedral | Trigonal bipyramidal | Octahedral |
| Zero Lone Pairs | Linear $AX_2$ | Trigonal planar $AX_3$ | Tetrahedral $AX_4$ | Trigonal bipyramidal $AX_5$ | Octahedral $AX_6$ |
| One Lone Pair | | Bent (V-shaped) $AX_2E$ | Trigonal pyramidal $AX_3E$ | Seesaw $AX_4E$ One axial lone pair | Square pyramidal $AX_5E$ |
| Two Lone Pairs | | | Bent (V-shaped) $AX_2E_2$ | T-shaped $AX_3E_2$ Two axial lone pairs | Square planar $AX_4E_2$ |
| Three Lone Pairs | | | | Linear $AX_2E_3$ Three axial lone pairs | |

This PheT applet will allow you to create all of the molecular shapes discussed above with and without lone pairs. You can investigate the structure of molecules, or of model shapes using VSEPR. By placing the cursor on any of the non central atoms or lone pairs you can rotate the molecules. You can add atoms and lone pairs to make any of VSEPR shapes




Click to Run

## Example 6

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. $PF_5$ (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. $H_30^+$ (hydronium ion)

**Given:** two chemical species

**Asked for:** molecular geometry

**Strategy:**

**A** Draw the Lewis electron structure of the molecule or polyatomic ion.

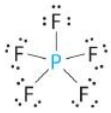
**B** Determine the electron group arrangement around the central atom that minimizes repulsions.

**C** Assign an $AX_mE_n$ designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

**D** Describe the molecular geometry.

**Solution:**

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of $PF_5$ is



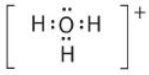
**B** There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 5.1.6 ).

**C** All electron groups are bonding pairs, so $PF_5$ is designated as $AX_5$. Notice that that gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

**D** The $PF_5$ molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



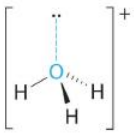
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



**B** There are four electron groups around oxygen, three bonding pairs and one lone pair. Like $NH_3$, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

**C** With three bonding pairs and one lone pair, the structure is designated as $AX_3E$ and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

**D** There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. $XeO_3$
2. $PF_6^-$
3. $NO_2^+$

**Answer**

1. trigonal pyramidal
2. octahedral
3. linear

## Example 7

Predict the molecular geometry of each molecule.

1. $XeF_2$
2. $SnCl_2$

**Given:** two chemical compounds

**Asked for:** molecular geometry

**Strategy:**

Use the strategy given in Example 1.

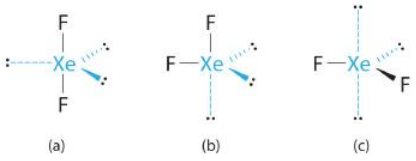
**Solution:**

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



**B** There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

**C** From B, $XeF_2$ is designated as $AX_2E_3$ and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:

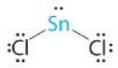



| Interactions | | | |
|---|---|---|---|
| 90 LP–LP | 0 | 2 | 2 |

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in $I_3^-$. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

**D** With two nuclei about the central atom, the molecular geometry of $XeF_2$ is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



**B** There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

**C** From B we designate $SnCl_2$ as $AX_2E$. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

**D** With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like $SO_2$, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise

Predict the molecular geometry of each molecule.

1. $SO_3$
2. $XeF_4$

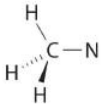
**Answers:**

1. trigonal planar
2. square planar

## Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked $AX_mE_n$ fragments. We will demonstrate with methyl isocyanate ($CH_3$–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked $AX_mE_n$ fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to $AX_4$. We can therefore predict the $CH_3$–N portion of the molecule to be roughly tetrahedral, similar to methane:

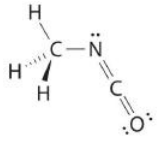



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



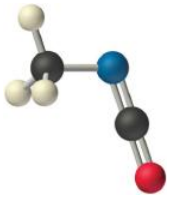

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:




We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120°. The experimentally determined structure of methyl isocyanate confirms our prediction (Figure 6.3.7 ).

**Figure 6.3.7 The Experimentally Determined Structure of Methyl Isocyanate**



Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in $CO_2$, so its geometry, like that of $CO_2$, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

## Example 8

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

**Given:** chemical compound

**Asked for:** molecular geometry

**Strategy:**

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 5.1.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

**Solution:**

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

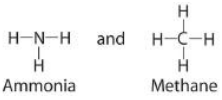
**Answer:** The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

## Molecular Representations

The structural formula for water can be drawn as follows, but including the two lone pairs on the oxygen provides more information:

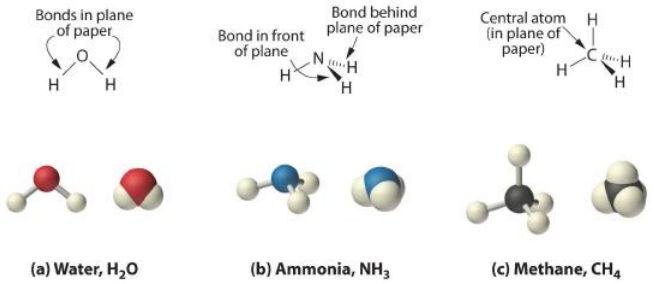



Because as we learned from VSEPR, the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia ($NH_3$) and methane ($CH_4$) are often written as planar molecules but at least for ammonia, it would be more informative to include the lone pair on the nitrogen atom:




As shown in Figure 6.4.8, however, we know that the the actual three-dimensional structure of $NH_3$ looks like a pyramid with a triangular base of three hydrogen atoms. Again using VSEPR, or what we know about sp3 orbitals on the central atom in all three molecules the structure of $CH_4$, with four hydrogen atoms arranged around a central carbon atom as shown in Figure 6.3.8 , is *tetrahedral*. That is, the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.

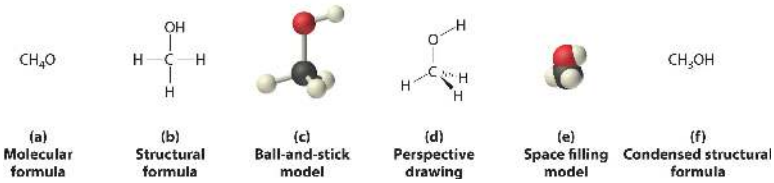
**Figure 6.3.8 The Three-Dimensional Structures of Water, Ammonia, and Methane**




*(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*

Figure 6.3.8 , illustrates different ways to represent the structures of molecules. It should be clear that there is no single “best” way to draw the structure of a molecule; the method you use depends on which aspect of the structure you want to emphasize and how much time and effort you want to spend. Figure 6.3.9 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (part (a) in Figure 6.3.9 ) gives only the number of each kind of atom; writing methanol as $CH_4O$ tells nothing about its structure. In contrast, the structural formula (part (b) in Figure 6.4.9 ) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 6.3.9 ) and the perspective drawing (part (d) in Figure 6.3.9 ) show the three-dimensional structure of the molecule. The latter (also called a *wedge-and-dash* representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 6.39 ) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. Also, in a space-filling model, atoms at the “front” of the molecule may obscure atoms at the “back.”

**Figure 6.4.9 Different Ways of Representing the Structure of a Molecule**




*(a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.*

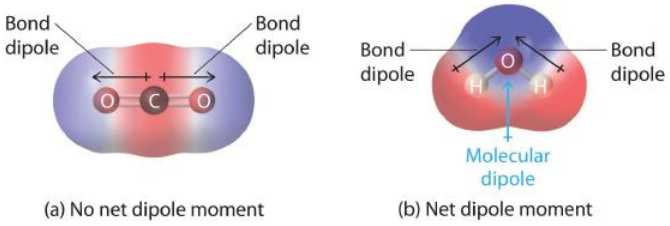
Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a *condensed structural formula* (part (f) in Figure 6.3.9 ), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is $CH_3OH$, which tells us that the molecule contains a $CH_3$ unit that looks like a fragment of methane ($CH_4$). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-

dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

## Molecular Dipole Moments

In Chapter 4 , you learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for $CO_2$, a linear molecule (part (a) in Figure 6.3.10 ). Each C–O bond in $CO_2$ is polar, yet experiments show that the $CO_2$ molecule has no dipole moment. Because the two C–O bond dipoles in $CO_2$ are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the $CO_2$ molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the $H_2O$ molecule is not linear (part (b) in Figure 6.3.10 ); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as $H_2O$ has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows $H_2O$ to hydrogen-bond to other polarized or charged species, including other water molecules.

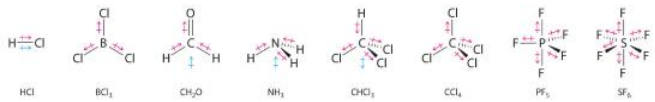
**Figure 6.3.10 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures**




*(a) In $CO_2$, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so $CO_2$ therefore has no net dipole. (b) In $H_2O$, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and $H_2O$ has a net dipole moment.*

Other examples of molecules with polar bonds are shown in Figure 6.3.11 "Molecules with Polar Bonds". In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

**Figure 6.3.11 Molecules with Polar Bonds**



Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, $CH_2O$, $NH_3$, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel ($BCl_3$, $CCl_4$, $PF_5$, and $SF_6$).

## Note the Pattern

Molecules with asymmetrical charge distributions have a net dipole moment.

## Example 9

Which molecule(s) has a net dipole moment?

1. $H_2S$
2. $NHF_2$
3. $BF_3$

**Given:** three chemical compounds

**Asked for:** net dipole moment

**Strategy:**

For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

**Solution:**

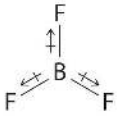
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of $H_2S$ is bent (Figure 6.3.6 ). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.




2. *Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of $NHF_2$ cannot cancel one another. This means that $NHF_2$ has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.*




3. *The molecular geometry of $BF_3$ is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus $BF_3$ has a net dipole moment of zero:*




Exercise

Which molecule(s) has a net dipole moment?

1. $CH_3Cl$
2. $SO_3$
3. $XeO_3$

**Answer:** $CH_3Cl$; $XeO_3$

## Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron

pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an $AX_mE_n$ designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. A combination of VSEPR and a bonding model, such as Lewis electron structures, however, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

## Key Takeaway

- The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds.

## Conceptual Problems

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: $AX_2$, $AX_2E$, and $AX_2E_2$. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom—$H_2S$ or $SiH_4$? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?
7. When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
8. How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
9. Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
10. How is molecular geometry related to the presence or absence of a molecular dipole moment?
11. How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
12. What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is $COF_2$ likely to have a significant dipole moment? Explain your answer.
13. When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
14. Use the VSPER model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.
    1. $CH_3Cl$
    2. $PCl_3$

3. CO
4. $SF_6$
5. $IF_5$
6. $CH_3OCH_3$
7. $CCl_3H$
8. $H_3COH$

15. The idealized molecular geometry of $BrF_5$ is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of $BrF_5$? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of $BrF_5$?
16. Which has the smallest bond angle around the central atom—$H_2S$, $H_2Se$, or $H_2Te$? the largest? Justify your answers.
17. Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

## Answers

1.
2.
3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.
4.
5.
6.
7.
8.
9.
10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.
14.
15.
16.
17.

## Numerical Problems

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. $BF_3$
    2. $PCl_3$
    3. $XeF_2$
    4. $AlCl_4^-$

5. $CH_2Cl_2$

2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.

    1. $ICl_3$
    2. $CCl_3^+$
    3. $H_2Te$
    4. $XeF_4$
    5. $NH_4^+$

3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

    1. HCl
    2. $NF_3$
    3. $ICl_2^+$
    4. $N_3^-$
    5. $H_3O^+$

4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

    1. $SO_3$
    2. $NH_2^-$
    3. $NO_3^-$
    4. $I_3^-$
    5. $OF_2$

5. What is the molecular geometry of $ClF_3$? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

6. Predict the molecular geometry of each of the following.

    1. $ICl_3$
    2. $AsF_5$
    3. $NO_2^-$
    4. $TeCl_4$

7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    1. NO
    2. HF
    3. $PCl_3$
    4. $CO_2$
    5. $SO_2$
    6. $SF_4$

8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    1. $OF_2$
    2. $BCl_3$
    3. $CH_2Cl_2$
    4. $TeF_4$
    5. $CH_3OH$
    6. $XeO_4$

9. Of the molecules $Cl_2C{=}Cl_2$, $IF_3$, and $SF_6$, which has a net dipole moment? Explain your reasoning.

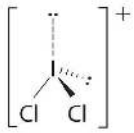
10. Of the molecules $SO_3$, $XeF_4$, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

## Answers

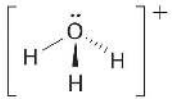
1. 1. trigonal planar (all electron groups are bonding pairs)
   2. tetrahedral (one lone pair on P)
   3. trigonal bipyramidal (three lone pairs on Xe)
   4. tetrahedral (all electron groups on Al are bonding pairs)
   5. tetrahedral (all electron groups on C are bonding pairs)
2. 
3. 1. four electron groups, linear molecular geometry
   2. four electron groups, pyramidal molecular geometry

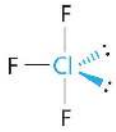



   3. four electron groups, bent molecular geometry



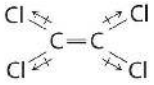

   4. two electron groups, linear molecular geometry
   5. four electron groups, pyramidal molecular geometry



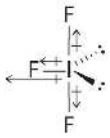

4. 
5. 


   The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

6. 
7. 
8. 
9. $Cl_2C{=}CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.




   $IF_3$: In this structure, the individual I–F bond dipoles cannot cancel one another, giving $IF_3$ a net dipole moment.




   $SF_6$: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, $SF_6$ has no net dipole moment.




10.

## Contributors

- Anonymous

Modified by Joshua Halpern

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# 9.3: Hybrid Orbitals

**Learning Objectives**

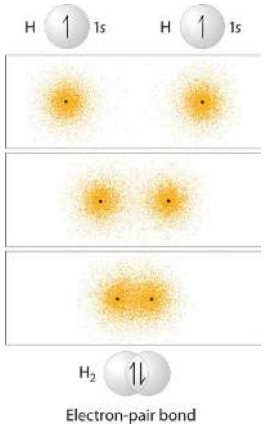
- To describe the bonding in simple compounds using valence bond theory.

Lewis structures provide no information about the shapes of molecules, being limited to which atoms are connected to each other and whether bonds are single, double or triple. A more sophisticated treatment of bonding is needed to begin to understand the shapes of molecules. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds. Using this model we will be able to predict the shapes of the molecules.

## Valence Bond Theory: A Localized Bonding Approach

In Chapter 4, you learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm ( Figure 4.4.2). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a maximum of two electrons with opposite spin, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 6.2.1).

**Figure 6.2.1 Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in $H_2$**



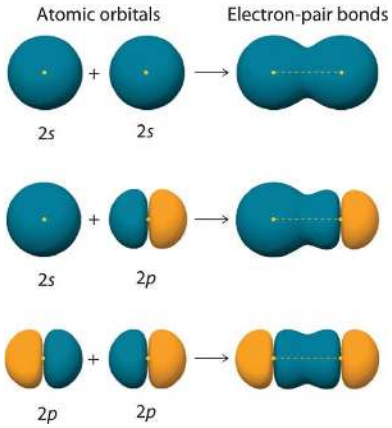

*The formation of $H_2$ from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an $H_2$ molecule increases the electron density in the region between the two positively charged nuclei.*

Although Lewis structures also contain localized electron-pair bonds, it does not use an atomic orbital approach to predict the stability and direction of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory (A localized bonding model that assumes that the strength of a covalent bond is proportional to the amount of overlap between atomic orbitals and that an atom can use different combinations of atomic orbitals (hybrids) to maximize the overlap between bonded atoms.), which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 6.2.2 shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

Figure 6.2.2 Three Different Ways to Form an Electron-Pair Bond




*An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.*

Let's examine the bonds in $BeH_2$, for example. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion (The excitation of an electron from a filled $ns^2$ to an *nsnp* valence orbital):




In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce $BeH_2$, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as $BeH_2$ form, scientists developed the concept of hybridization.

## Hybridization of *s* and *p* Orbitals

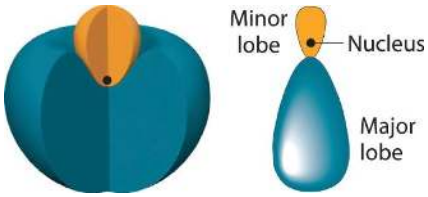
The localized bonding approach uses a process called hybridization (A process in which two or more atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds), in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitalsNew atomic orbitals formed from the process of hybridization. because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

In $BeH_2$, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 6.2.3. Because the difference A − B can also be written as A + (−B), in Figure 6.2.3 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as

multiplying it by −1 and adding. This gives us Equation 6.2.1, where the value $1/\sqrt{2}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

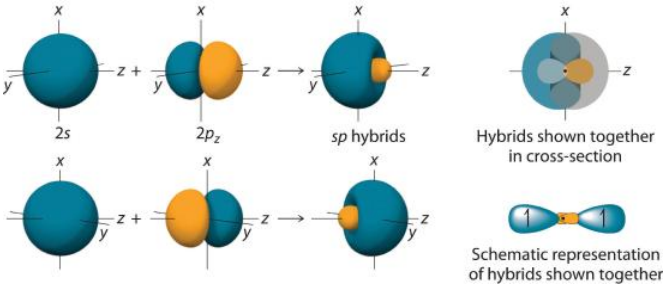
$$sp_1 = \frac{1}{\sqrt{2}}(2s + 2p_z) \quad and \quad sp_2 = \frac{1}{\sqrt{2}}(2s - 2p_z)$$

Generally we do not use the subsript labels on the two *sp* orbitals, but we have done so here to emphasize that there are two different orbitals. It is also important to remember that the two *sp* orbitals are built from orbitals of the same atom and centered on the nucleus of that atom. Later in this chapter we will meet molecular orbitals which are linear combinations of atomic orbitals (LCAO in theoretical chemistry speak) centered on *different* atoms. It is often difficult for students to figure out the difference



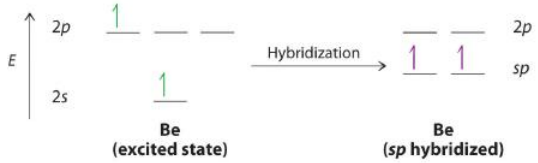

***The position of the atomic nucleus with respect to an sp hybrid orbital.*** *The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.*

**Figure 6.2.3 The Formation of *sp* Hybrid Orbitals**



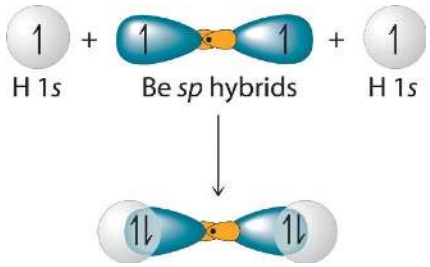

*Taking the mathematical sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180° to each other.*

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:




This indicates that each *sp* hybrid orbital is singly occupied and can bond with a 1s electron of a hydrogen atom. (The two equivalent hybrid orbitals result when one *ns* orbital and one *np* orbital are combined (hybridized)). The two *sp* hybrid orbitals are oriented at 180° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals. They can now form an electron-pair bond with the singly occupied 1*s* atomic orbital of one of the H atoms. As shown in Figure 6.2.4, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear $BeH_2$ molecule. Thus valence bond theory does what the Lewis electron structurel is able to do; it explains why the bonds in $BeH_2$ are equivalent in energy and why $BeH_2$ has a linear geometry.

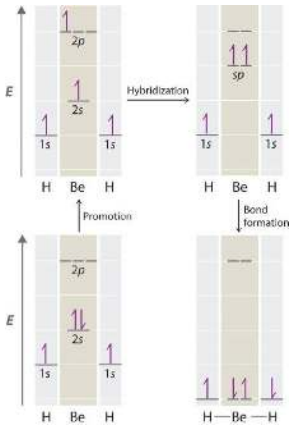
**Figure 6.2.4 Explanation of the Bonding in $BeH_2$ Using *sp* Hybrid Orbitals**




*Each singly occupied sp hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two sp hybrid orbitals are oriented at a 180° angle, the $BeH_2$ molecule is linear.*

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 6.1.5 ). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

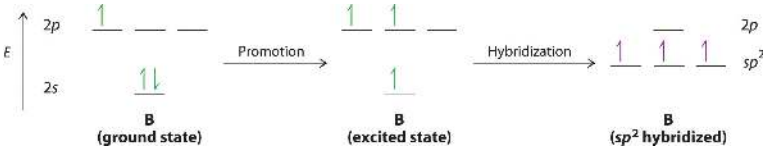
**Figure 6.2.5 A Hypothetical Stepwise Process for the Formation of $BeH_2$ from a Gaseous Be Atom and Two Gaseous H Atoms**




*The promotion of an electron from the 2s orbital of beryllium to one of the 2p orbitals is energetically uphill. The overall process of forming a $BeH_2$ molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.*

The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce $BF_3$. The Lewis approach only works on the assumption that molecules with a central atom having LESS than an octet can exist. You may remember that this was one of the handwaves that we had to introduce in the previous chapter discussing Lewis structures.

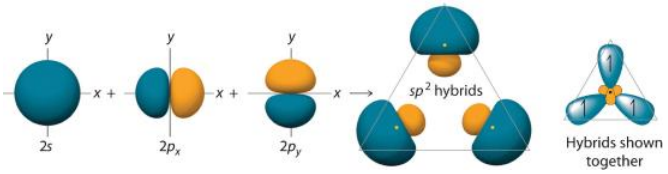
With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:




The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure 6.2.6). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be $sp^2$ *hybridized* (pronounced “s-p-two” or “s-p-squared”). The singly occupied $sp^2$ hybrid atomic orbitalsThe three equivalent hybrid orbitals that result when one *ns* orbital and two np orbitals are combined (hybridized). The three $sp^2$ hybrid orbitals are oriented in a plane at 120° from each other. They are equivalent in energy,

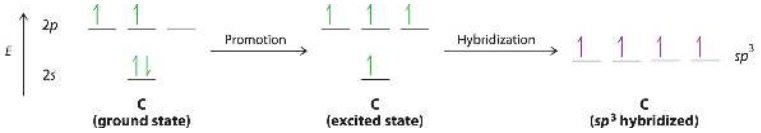
and their energy is between the energy values associated with pure s and pure p orbitals. can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

**Figure 6.2.6 Formation of $sp^2$ Hybrid Orbitals**




*Combining one ns and two np atomic orbitals gives three equivalent $sp^2$ hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.*

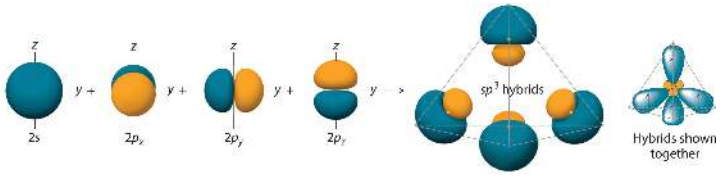
Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate $sp^3$ ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:




The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 6.2.7). It is rather difficult to visualize a tetrahedron. A simple, though inelegant way of doing so is to stand with one foot forward and the other backwards. Now raise your hands from your sides to above your shoulders.

Like all the hybridized orbitals discussed earlier, the $sp^3$ hybrid atomic orbitals (The four equivalent hybrid orbitals that result when one *ns* orbital and three *np* orbitals are combined (hybridized). The four $sp^3$ hybrid orbitals point at the vertices of a tetrahedron, so they are oriented at 109.5° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure *s* and pure *p* orbitals. are predicted to be equal in energy.

**Figure 6.2.7 Formation of $sp^3$ Hybrid Orbitals**




*Combining one ns and three np atomic orbitals results in four $sp^3$ hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.*

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as $CH_2$ or $CF_2$), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

### Note the Pattern

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as $NH_3$ or $H_2O$, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In $NH_3$, for example, N, with a $2s^22p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four $sp^3$ hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:




The three singly occupied $sp^3$ lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, $H_2O$ has an $sp^3$ hybridized oxygen atom that uses two singly occupied $sp^3$ lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in $NH_3$ and $H_2O$. Unfortunately, however, recent experimental evidence indicates that in $CH_4$ and $NH_3$, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

### Example 3

Predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

1. $H_2S$
2. $CHCl_3$

**Given:** two chemical compounds

**Asked for:** number of electron pairs and molecular geometry, hybridization, and bonding

**Strategy:**

**A** Using the approach from Example 1, determine the number of electron pairs and the molecular geometry of the molecule.

**B** From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

**Solution:**

1. **A** $H_2S$ has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four $sp^3$ hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two $sp^3$ hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four $sp^3$ hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four $sp^3$ hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three $sp^3$ hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as $sp^3$ hybridized. Each Cl atom uses a singly occupied $sp^3$ hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise

Predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

1. the $BF_4^-$ ion
2. hydrazine ($H_2N–NH_2$)

**Answer**

1. B is $sp^3$ hybridized; F is also $sp^3$ hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.
2. Each N atom is $sp^3$ hybridized and uses one $sp^3$ hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

### Note the Pattern

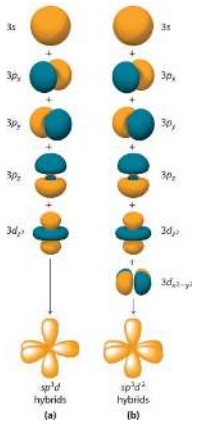
The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

## Hybridization Using *d* Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in $PF_5$ and $SF_6$). Using the *ns* orbital, all three *np* orbitals, and one $(n - 1)d$ orbital gives a set of five $sp^3d$ hybrid orbitals (The five hybrid orbitals that result when one *s* three *p* and one *d* orbitals are combined (hybridized)). that point toward the vertices of a trigonal bipyramid (part (a) in Figure 5.17 ). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent $sp^3d^2$ hybrid orbitals (The six equivalent hybrid orbitals that result when one *s*, three p, and two d orbitals are combined (hybridized). oriented toward the vertices of an octahedron (part (b) in Figure 6.2.8). In the VSEPR model, $PF_5$ and $SF_6$ are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which $sp^3d$ or $sp^3d^2$ hybrid orbitals are used for bonding.

**Figure 6.2.8 Hybrid Orbitals Involving *d* Orbitals**




*The formation of a set of (a) five $sp^3d$ hybrid orbitals and (b) six $sp^3d^2$ hybrid orbitals from ns, np, and nd atomic orbitals where n = 4.*

### Example 4

What is the hybridization of the central atom in each species? Describe the bonding in each species.

1. $XeF_4$
2. $SO_4^{2-}$
3. $SF_4$

**Given:** three chemical species

**Asked for:** hybridization of the central atom

**Strategy:**

**A** Determine the geometry of the molecule using the strategy in Example 1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.

**B** Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

**Solution:**

1. **A** Xe in $XeF_4$ forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be $sp^3d^2$ hybridized. **B** With 12 electrons around Xe, four of the six $sp^3d^2$ hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
2. **A** The S in the $SO_4^{2-}$ ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be $sp^3$ hybridized to generate four S–O bonds. **B** Filling the $sp^3$ hybrid orbitals with eight electrons from four bonds produces four filled $sp^3$ hybrid orbitals.
3. **A** The S atom in $SF_4$ contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:




To accommodate five electron pairs, the sulfur atom must be $sp^3d$ hybridized. **B** Filling these orbitals with 10 electrons gives four $sp^3d$ hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise

What is the hybridization of the central atom in each species? Describe the bonding.

1. $PCl_4^+$
2. $BrF_3$
3. $SiF_6^{2-}$

**Answer**

1. $sp^3$ with four P–Cl bonds
2. $sp^3d$ with three Br–F bonds and two lone pairs
3. $sp^3d^2$ with six Si–F bonds

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides ($CF_4$ and $SiF_4$), only $SiF_4$ reacts with $F^-$ to give a stable hexafluoro dianion, $SiF_6^{2-}$. Because there are no 2*d* atomic orbitals, the formation of octahedral $CF_6^{2-}$ would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of $sp^3d^2$ hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as $CF_6^{2-}$ have never been prepared.

## Example 5

What is the hybridization of the oxygen atom in $OF_4$? Is $OF_4$ likely to exist?

**Given:** chemical compound

**Asked for:** hybridization and stability

**Strategy:**

**A** Predict the geometry of $OF_4$ using the VSEPR model.

**B** From the number of electron pairs around O in $OF_4$, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

**Solution:**

**A** T $OF_4$ will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be $sp^3d$ hybridized. The only *d* orbital available for forming a set of

$sp^3d$ hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the $OF_4$ molecule is unlikely to exist. In fact, it has not been detected.

Exercise

What is the hybridization of the boron atom in $BF_6^{3-}$? Is this ion likely to exist?

**Answer:** $sp^3d^2$ hybridization; no

## Summary

The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled $ns^2$ subshell to an empty *np* or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent $\boldsymbol{sp^2}$ **hybrids** or four equivalent $\boldsymbol{sp^3}$ **hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five $sp^3d$ or six $\boldsymbol{sp^3d^2}$ **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

## Key Takeaway

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

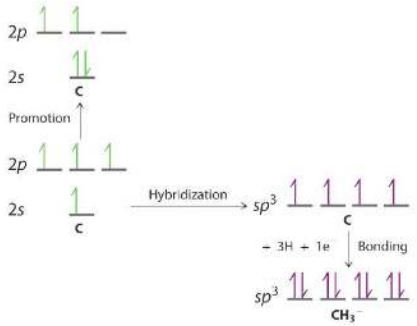
## Conceptual Problems

1. Arrange *sp*, $sp^3$, and $sp^2$ in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.
2. What atomic orbitals are combined to form $sp^3$, *sp*, $sp^3d^2$, and $sp^3d$? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?
3. Why is it incorrect to say that an atom with $sp^2$ hybridization will form only three bonds? The carbon atom in the carbonate anion is $sp^2$ hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?
4. If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?
5. How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?
6. In the valence bond approach to bonding in $BeF_2$, which step(s) require(s) an energy input, and which release(s) energy?
7. The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?
8. How are lone pairs on the central atom treated using hybrid orbitals?
9. Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use $sp^2$ hybrid orbitals instead of $sp^3$ hybrids?
10. Using arguments based on orbital hybridization, explain why the $CCl_6^{2-}$ ion does not exist.
11. Species such as $NF_5^{2-}$ and $OF_4^{2-}$ are unknown. If 3*d* atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

## Numerical Problems

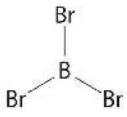
1. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in $CH_3^-$. How does your diagram compare with that for methane? What is the molecular geometry?
2. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in $CH_3^+$. How does your diagram compare with that for methane? What is the molecular geometry?
3. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.
    1. $BBr_3$
    2. $PCl_3$
    3. $NO_3^-$
4. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.
    1. $AsBr_3$
    2. $CF_3^+$
    3. $H_2O$
5. What is the hybridization of the central atom in each of the following?
    1. $CF_4$
    2. $CCl_2^{2-}$
    3. $IO_3^-$
    4. $SiH_4$
6. What is the hybridization of the central atom in each of the following?
    1. $CCl_3^+$
    2. $CBr_2O$
    3. $CO_3^{2-}$
    4. $IBr_2^-$
7. What is the hybridization of the central atom in $PF_6^-$? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?
8. What is the hybridization of the central atom in $SF_5^-$? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

## Answers

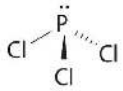
1. 


   The promotion and hybridization process is exactly the same as shown for $CH_4$ in the chapter. The only difference is that the C atom uses the four singly occupied $sp^3$ hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1–. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in $NH_3$.

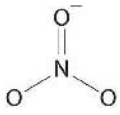
2.

3. 1. 


   $sp^2$, trigonal planar

   2. 


   $sp^3$, pyramidal

   3. 


   $sp^2$, trigonal planar

4.

5. The central atoms in $CF_4$, $CCl_2^{2-}$, $IO_3^-$, and $SiH_4$ are all $sp^3$ hybridized.

6.

7. The phosphorus atom in the $PF_6^-$ ion is $sp^3d^2$ hybridized, and the ion is octahedral. The $PF_6^-$ ion is isoelectronic with $SF_6$ and has essentially the same structure. It should therefore be a stable species.

8.

## Contributors

- Anonymous

Modified by Joshua Halpern

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# 9.4: Delocalized Bonding and Molecular Orbitals

**Learning Objectives**

- To understand "resonance structures"
- To use molecular orbital theory to predict bond order.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

In Chapter 2, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory A delocalized bonding model in which molecular orbitals are created from the linear combination of atomic orbitals (LCAOs), is a *delocalized* approach to bonding.

### Note the Pattern

Molecular orbital theory is a delocalized bonding approach that explains the colors of compounds, their stability, and resonance.

### Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

### Molecular Orbitals Involving Only *ns* Atomic Orbitals

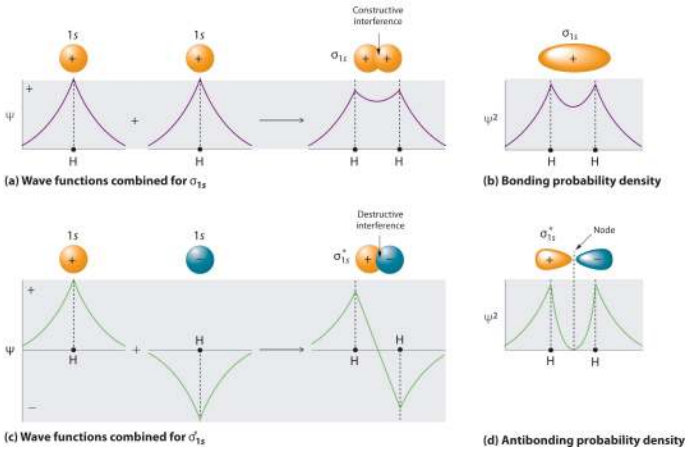
We begin our discussion of molecular orbitals with the simplest molecule, $H_2$, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 2 electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. (For more information on wave functions, see Section 2.5) The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+ &\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &- &\quad AO(atom B) \end{aligned}$$

The molecular orbitals created from Equation 6.5.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a $\sigma_{1s}$ combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 6.5.1 ). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived:The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

**Figure 6.5.1 Molecular Orbitals for the $H_2$ Molecule**




*(a) This diagram shows the formation of a bonding $\sigma_{1s}$ molecular orbital for $H_2$ as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function ($\Psi^2$) for the bonding $\sigma_{1s}$ molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall from Chapter 2 that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding $\sigma^*_{1s}$ molecular orbital for $H_2$ as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function ($\Psi^2$) for the $\sigma^*_{1s}$ antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.*

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B)$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 6.5.1 ). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called $\sigma^*_{1s}$ ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B)$$

### Note the Pattern

A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the $\sigma_{1s}$ molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the $\sigma_{1s}$ orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^*_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^*_{1s}$ orbital is an antibonding molecular orbital A molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructuve reinforcement of the wave functions..

### Note the Pattern

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

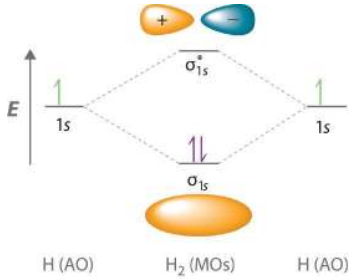
### Energy-Level Diagrams

Because electrons in the $\sigma_{1s}$ orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the $\sigma_{1s}$ molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^*_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^*_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The $\sigma_{1s}$ (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^*_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram A schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals. in Figure 6.5.2

### Note the Pattern

A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

**Figure 6.5.2 Molecular Orbital Energy-Level Diagram for $H_2$**




*The two available electrons (one from each H atom) in this diagram fill the bonding $\sigma_{1s}$ molecular orbital. Because the energy of the $\sigma_{1s}$ molecular orbital is lower than that of the two H 1s atomic orbitals, the $H_2$ molecule is more stable (at a lower energy) than the two isolated H atoms.*

To describe the bonding in a homonuclear diatomic molecule A molecule that consists of two atoms of the same element. such as $H_2$, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 6.5.2 ). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the $\sigma_{1s}$ bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the $H_2$ molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that $H_2$ is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

## Bond Order in Molecular Orbital Theory

In the Lewis electron structures described in Chapter 4 , the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2}$$

To calculate the bond order of $H_2$, we see from Figure 6.5.2 that the $\sigma_{1s}$ (bonding) molecular orbital contains two electrons, while the $\sigma^*_{1s}$ (antibonding) molecular orbital is empty. The bond order of $H_2$ is therefore

$$\frac{2-0}{2} = 1$$

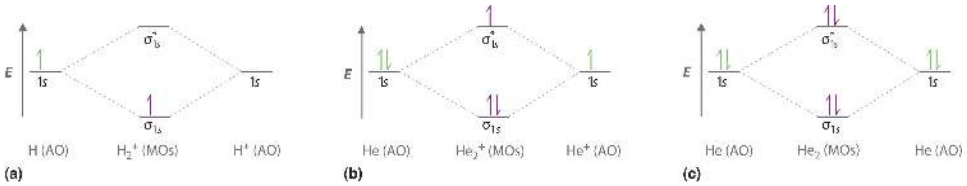
This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 6.5.2 to describe the bonding in other pairs of atoms and ions where $n$ = 1, such as the $H_2^+$ ion, the $He_2^+$ ion, and the $He_2$ molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

Part (a) in Figure 6.5.3 shows the energy-level diagram for the $H_2^+$ ion, which contains two protons and only one electron. The single electron occupies the $\sigma_{1s}$ bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the $H_2^+$ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as $H_2^+$. With a bond order of only 1/2 the bond in $H_2^+$ should be weaker than in the $H_2$ molecule, and the H–H bond should be longer. As shown in Table 6.5.1 , these predictions agree with the experimental data.

Part (b) in Figure 5.3.3 is the molecular orbital energy-level diagram for $He_2^+$. This ion has a total of three valence electrons. Because the first two electrons completely fill the $\sigma_{1s}$ molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^*_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2\,(\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with $H_2^+$, the $He_2^+$ ion should be stable, but the He–He bond should be weaker and longer than in $H_2$. In fact, the $He_2^+$ ion can be prepared, and its properties are consistent with our predictions (Table 6.5.1 ).

**Figure 6.5.3 Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals**



*(a) The $H_2^+$ ion, (b) the $He_2^+$ ion, and (c) the $He_2$ molecule are shown here.*

**Table 6.5.1 Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions**

| Molecule or Ion | Electron Configuration | Bond Order | Bond Length (pm) | Bond Energy (kJ/mol) |
|---|---|---|---|---|
| $H_2^+$ | $(\sigma_{1s})^1$ | 1/2 | 106 | 269 |
| $H_2$ | $(\sigma_{1s})^2$ | 1 | 74 | 436 |
| $He_2^+$ | $(\sigma_{1s})^2(\sigma^*_{1s})^1$ | 1/2 | 108 | 251 |
| $He_2$ | $(\sigma_{1s})^2(\sigma^*_{1s})^2$ | 0 | not observed | not observed |

Finally, we examine the $He_2$ molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 6.5.3 is the molecular orbital energy-level diagram for $He_2$. With a total of four valence electrons, both the $\sigma_{1s}$ bonding and $\sigma^*_{1s}$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the $He_2$ molecule has no net bond and is not a stable species. Experiments show that the $He_2$ molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the $H_2^+$ ion.

### Note the Pattern

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

### Example 11

Use a molecular orbital energy-level diagram, such as those in Figure 6.5.3 , to predict the bond order in the $He_2^{2+}$ ion. Is this a stable species?

**Given:** chemical species

**Asked for:** molecular orbital energy-level diagram, bond order, and stability

**Strategy:**

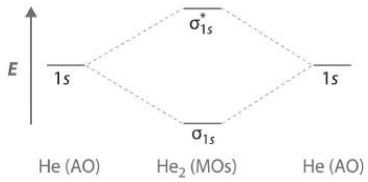
**A** Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.

**B** Determine the total number of valence electrons in the $He_2^{2+}$ ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

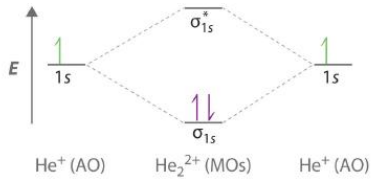
**C** Calculate the bond order and predict whether the species is stable.

**Solution:**

**A** Two He 1*s* atomic orbitals combine to give two molecular orbitals: a $\sigma_{1s}$ bonding orbital at lower energy than the atomic orbitals and a $\sigma^*_{1s}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:




**B** The $He_2^{2+}$ ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view $He_2^{2+}$ as being formed from two $He^+$ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:




The two electrons occupy the lowest-energy molecular orbital, which is the bonding ($\sigma_{1s}$) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2} = 1$$

$He_2^{2+}$ is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise

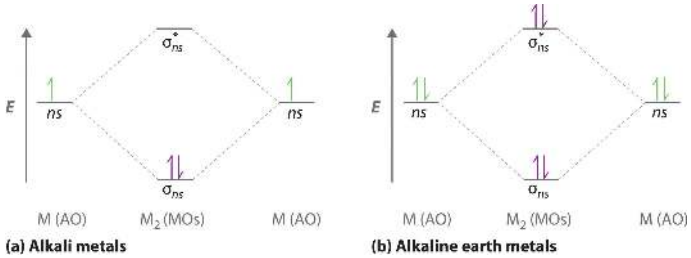
Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the $H_2^{2-}$ ion. Is this a stable species?

**Answer:** $H_2^{2-}$ has a valence electron configuration of $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms ($Li_2$ and $Cs_2$, for example) is shown in part (a) in Figure 6.5.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a $\sigma_{ns}$ bonding molecular orbital and a $\sigma^*_{ns}$ antibonding molecular orbital. Because each alkali metal (M) has an $ns^1$ valence electron configuration, the $M_2$ molecule has two valence electrons that fill the $\sigma_{ns}$ bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals ($Li_2$, $Na_2$, $K_2$, $Rb_2$, and $Cs_2$). The general features of these $M_2$ diagrams are identical to the diagram for the $H_2$ molecule in Figure 6.5.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

**Figure 6.5.4 Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic ($M_2$) Molecules**




*(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the $\sigma_{ns}$ (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the $\sigma_{ns}$ (bonding) and the $\sigma_{ns}$* (nonbonding) levels, leading to a predicted bond order of 0.*

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as $Be_2$), in which each metal atom has an $ns^2$ valence electron configuration, resemble the diagram for the $He_2$ molecule in part (c) in Figure 6.5.3 As shown in part (b) in Figure 6.5.4 , this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the $\sigma_{ns}$ bonding orbital and the $\sigma_{ns}$* antibonding orbital and give a bond order of 0. Thus $Be_2$, $Mg_2$, $Ca_2$, $Sr_2$, and $Ba_2$ are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, $Be_2$ is stable.

### Example 12

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the $Na_2^-$ ion.

**Given:** chemical species

**Asked for:** molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

**Strategy:**

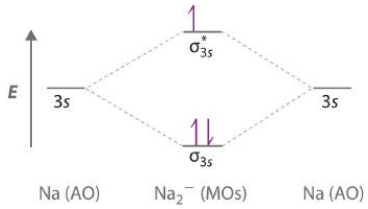
**A** Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

**B** Determine the total number of valence electrons in the $Na_2^-$ ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

**C** Calculate the bond order and predict whether the species is stable.

**Solution:**

**A** Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The $Na_2^-$ ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled $\sigma_{3s}$ molecular orbital, a half-filled $\sigma_{3s*}$ and a $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ electron configuration.




**C** The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the $Na_2^-$ ion exists but is highly reactive.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the $Ca_2^+$ ion.

**Answer:** $Ca_2^+$ has a $(\sigma_{4s})^2(\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

## Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall from Section 2.5 that for each *np* subshell, for example, there are $np_x$, $np_y$, and $np_z$ orbitals ( Figure 2.5.6). All have the same energy and are therefore degenerate, but they have different spatial orientations.$\sigma_{np_z} = np_z(A) - np_z(B)$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two $np_z$ atomic orbitals in part (a) in Figure 6.3.5, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a $\sigma_{np_z}$ *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

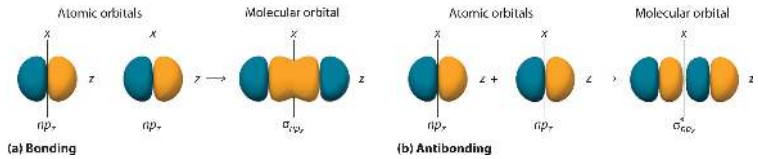
$$\sigma_{np_z} = np_z(A) - np_z(B)$$

The other possible combination of the two $np_z$ orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B)$$

In this combination, shown in part (b) in Figure 6.5.5, the positive lobe of one $np_z$ atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

**Figure 6.5.5 Formation of Molecular Orbitals from $np_z$ Atomic Orbitals on Adjacent Atoms**




*(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +z to the right. As a result, the signs of the lobes of the $np_z$ atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical difference, in which the overlap of lobes with the same sign results in increased probability density between the*

*nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical sum, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.*

### Note the Pattern

Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

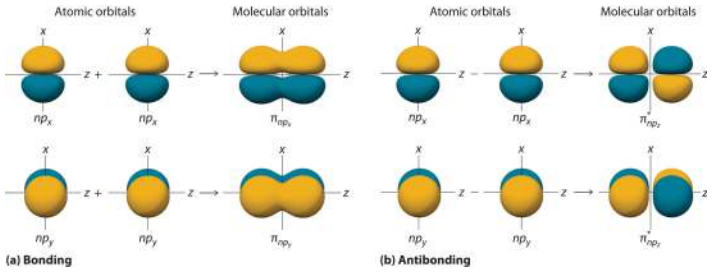
The remaining *p* orbitals on each of the two atoms, $np_x$ and $np_y$, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 6.5.6, we see that we have two pairs of *np* orbitals: the two $np_x$ orbitals lying in the plane of the page, and two $np_y$ orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the $np_x$ orbital on one atom can interact with only the $np_x$ orbital on the other, and the $np_y$ orbital on one atom can interact with only the $np_y$ on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbitalA bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals.. The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B)$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B)$$

The two $np_y$ orbitals can also combine using side-to-side interactions to produce a bonding $\pi_{np_y}$ molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the $np_x$ and $np_y$ atomic orbitals interact in the same way (side-to-side) and have the same energy, the $\pi_{np_z}$ and $\pi_{np_y}$molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

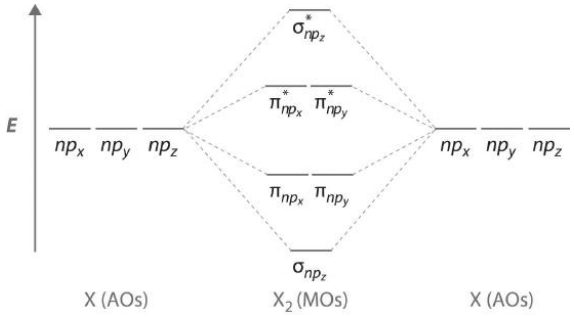
**Figure 6.5.6 Formation of π Molecular Orbitals from $np_x$ and $np_y$ Atomic Orbitals on Adjacent Atoms**




*(a) Because the signs of the lobes of both the $np_x$ and the $np_y$ atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.*

Figure 6.5.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

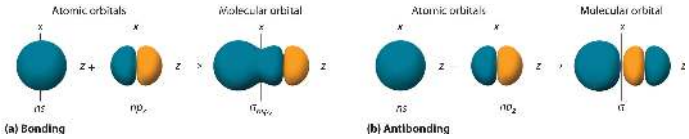
**Figure 6.5.7 The Relative Energies of the σ and π Molecular Orbitals Derived from $np_x$, $np_y$, and $np_z$ Orbitals on Identical Adjacent Atoms**



*Because the two $np_z$ orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.*

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an $np_z$ atomic orbital on another. As shown in Figure 6.5.8 , the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

**Figure 6.5.8 Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an $np_z$ Atomic Orbital on an Adjacent Atom**




*(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.*

## Molecular Orbital Diagrams for Period 2 Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as $N_2$, $O_2$, and $F_2$. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals A law that states that the number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

## Note the Pattern

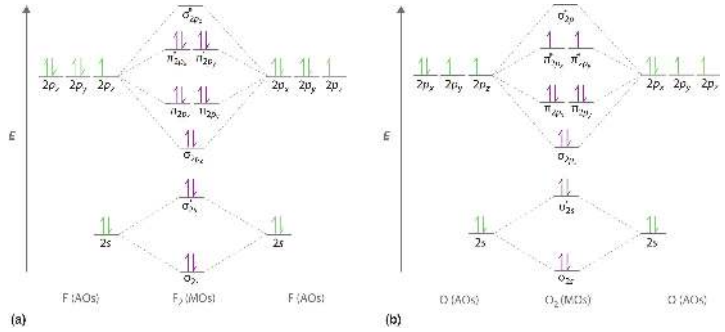
The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for $F_2$. We use the diagram in part (a) in Figure 6.5.9 ; the $n = 1$ orbitals ($\sigma_{1s}$ and $\sigma_{1s}$*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the $\sigma_{2s}$ and $\sigma_{2s}$* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is $\sigma_{2p_z}$ and the next most stable are the two degenerate orbitals, $\pi_{2p_x}$ and $\pi_{2p_y}$. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the $F_2$ molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the $\sigma_{2s}$ and $\sigma_{2s}$* orbitals, 2 fill the $\sigma_{2p_z}$ orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate $\pi^*$ orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts $F_2$ to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus $F_2$ is predicted to have a stable F–F single bond, in agreement with experimental data.

We now turn to a molecular orbital description of the bonding in $O_2$. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for $O_2$, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 6.5.9. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the $\sigma_{2s}$ and $\sigma_{2s}$* orbitals, 2 more to fill the $\sigma_{2p_z}$ orbital, and 4 to fill the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate $\pi^*$ orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

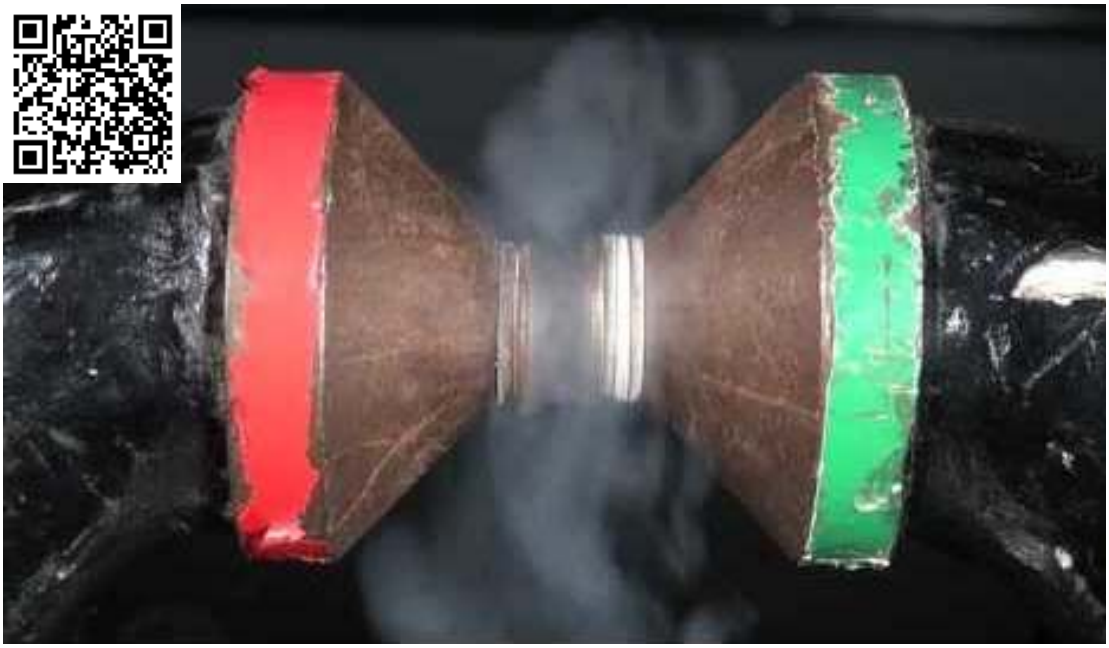
**Figure 6.5.9 Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules**



*(a) For $F_2$, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^{\star}_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For $O_2$, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the $O_2$ molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.*

None of the other bonding models can predict the presence of two unpaired electrons in $O_2$. Chemists had long wondered why, unlike most other substances, liquid $O_2$ is attracted into a magnetic field. As shown in Figure 6.5.10 , it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for $O_2$ to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

**Figure 6.5.10 Liquid $O_2$ Suspended between the Poles of a Magnet**



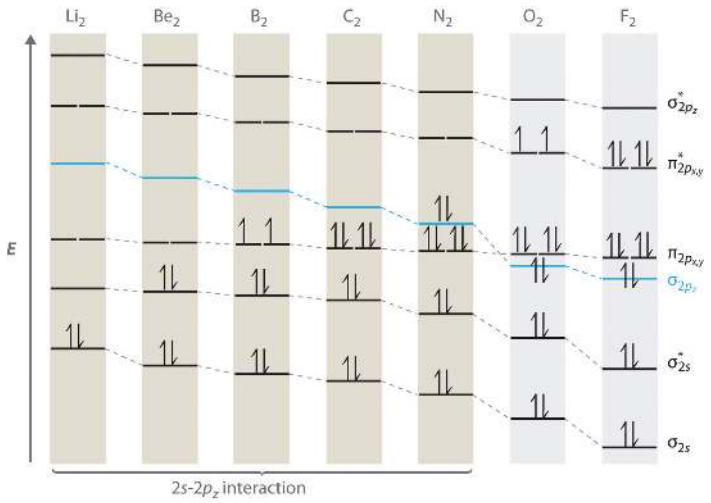
Because the $O_2$ molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

The magnetic properties of $O_2$ are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form $H_2O$, $CO_2$, and $N_2$ in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as $H_2O$, $CO_2$, and $N_2$, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of $O_2$ with organic compounds to give $H_2O$, $CO_2$, and $N_2$ would require that at least one of the electrons on $O_2$ change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of $N_2$ in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the $\sigma_{2p_z}$ molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p*

atomic orbitals increases from $Li_2$ to $F_2$ due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the $\sigma_{2s}$ orbital and increases the energy of the $\sigma_{2p_z}$ orbital. Thus for $Li_2$, $Be_2$, $B_2$, $C_2$, and $N_2$, the $\sigma_{2p_z}$ orbital is higher in energy than the $\sigma_{3p_z}$ orbitals, as shown in Figure 6.5.11 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 6.5.11 ). Thus for example, the $\sigma_{2p_z}$ molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

**Figure 6.5.11 Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements**




*Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For $Li_2$ through $N_2$, the $\sigma_{2p_z}$ orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the $\sigma_{2p_z}$ orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for $O_2$ and $F_2$ due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.*

Completing the diagram for $N_2$ in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in $N_2$ versus 141.2 pm in $F_2$), and the bond energy is much greater for $N_2$ than for $F_2$ (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the $N_2$ bond is much shorter and stronger than the $F_2$ bond, consistent with what we would expect when comparing a triple bond with a single bond.

### Example 13

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in $S_2$, a bright blue gas at high temperatures.

**Given:** chemical species

**Asked for:** molecular orbital energy-level diagram, bond order, and number of unpaired electrons

**Strategy:**

**A** Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in $S_2$. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.

**B** Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in $S_2$.

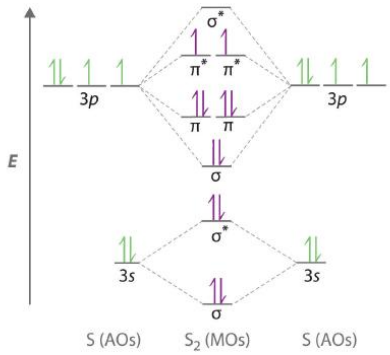
**C** Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.

**D** Calculate the bond order and describe the bonding.

**Solution:**

**A** Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 6.5.9 and Figure 6.5.11 , we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the $\sigma_{3p_z}$> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 5.3.11 ), the $\sigma_{3p_z}$ molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

**B** The molecular orbital energy-level diagram is as follows:




Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

**C** Ten valence electrons are used to fill the orbitals through $\pi_{3p_x}$ and $\pi_{3p_y}$, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_z}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of $S_2$ is $(\sigma_{3s})^2\,(\sigma^{\star}_{3s})^2\,(\sigma_{3p_z})^2\,(\pi_{3p_{x,y}})^4\,(\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise

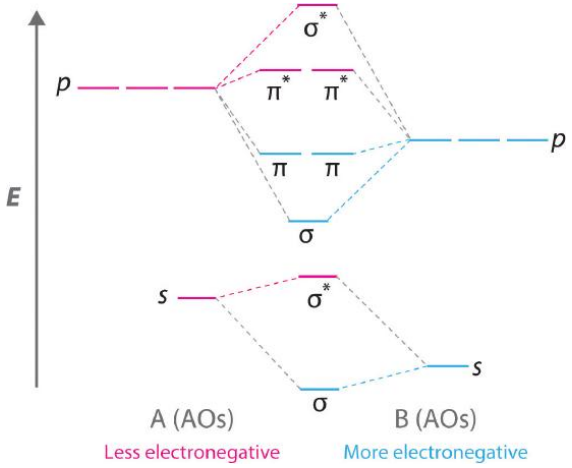
Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion ($O_2^{2-}$).

**Answer:** $(\sigma_{2s})^2\,(\sigma^{\star}_{2s})^2\,(\sigma_{2p_z})^2\,(\pi_{2p_{x,y}})^4\,(\pi_{2p^{\star}_{x,y}})^4$ bond order of 1; no unpaired electrons

## Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules A molecule that consists of two atoms of different elements.. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 6.5.12 . The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

**Figure 6.5.12 Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$**




The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

### Note the Pattern

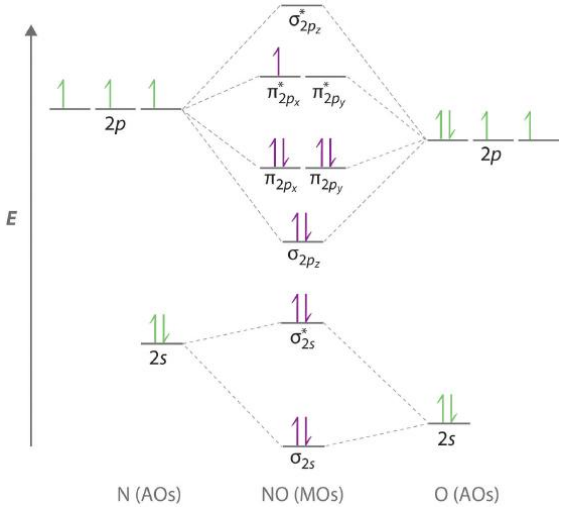
A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

## An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of $O_2$ with $N_2$ at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with $O_2$ to produce $NO_2$, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 6.5.13 ) shows that the general pattern is similar to that for the $O_2$ molecule (see Figure 6.5.11 ). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate $\pi^*$ orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the $N_2$ and $O_2$ molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

**Figure 6.5.13 Molecular Orbital Energy-Level Diagram for NO**



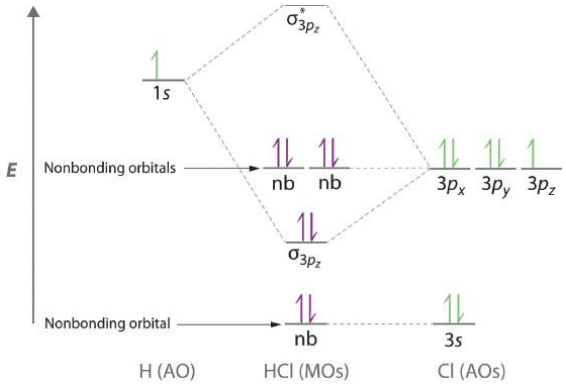

*Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the* $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ *pair of orbitals.*

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 6.5.13 , NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the $NO^+$ cation, which is isoelectronic with $N_2$ and has a bond order of 3, corresponding to an N≡O triple bond.

## Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 6.3.14 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called nonbonding molecular orbitals A molecular orbital that forms when atomic orbitals or orbital lobes interact only very weakly, creating essentially no change in the electron probability density between the nuclei.. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - -Cl^{\delta-}$

**Figure 6.5.14 Molecular Orbital Energy-Level Diagram for HCl**




*The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.*

### Note the Pattern

Electrons in nonbonding molecular orbitals have no effect on bond order.

### Example 14

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 6.5.12 to describe the bonding in the cyanide ion ($CN^-$). What is the bond order?

**Given:** chemical species

**Asked for:** "skewed" molecular orbital energy-level diagram, bonding description, and bond order

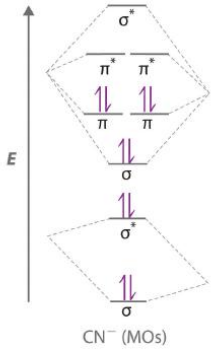
**Strategy:**

**A** Calculate the total number of valence electrons in $CN^-$. Then place these electrons in a molecular orbital energy-level diagram like Figure 6.5.12 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

**B** Calculate the bond order and describe the bonding in $CN^-$.

**Solution:**

**A** The $CN^-$ ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 6.5.12 fills the five lowest-energy orbitals, as shown here:




Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the $CN^-$ ion has a triple bond, analogous to that in $N_2$.

Exercise

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion ($OCl^-$). What is the bond order?

**Answer:** All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

## Summary

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the $O_2$ molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

## Key Takeaway

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

## Conceptual Problems

1. What is the distinction between an atomic orbital and a molecular orbital? How many electrons can a molecular orbital accommodate?
2. Why is the molecular orbital approach to bonding called a *delocalized* approach?
3. How is the energy of an electron affected by interacting with more than one positively charged atomic nucleus at a time? Does the energy of the system increase, decrease, or remain unchanged? Why?
4. Constructive and destructive interference of waves can be used to understand how bonding and antibonding molecular orbitals are formed from atomic orbitals. Does constructive interference of waves result in increased or decreased electron probability density between the nuclei? Is the result of constructive interference best described as a bonding molecular orbital or an antibonding molecular orbital?
5. What is a "node" in molecular orbital theory? How is it similar to the nodes found in atomic orbitals?
6. What is the difference between an *s* orbital and a σ orbital? How are the two similar?

7. Why is a $\sigma_{1s}$ molecular orbital lower in energy than the two *s* atomic orbitals from which it is derived? Why is a $\sigma^*_{1s}$ molecular orbital higher in energy than the two *s* atomic orbitals from which it is derived?
8. What is meant by the term *bond order* in molecular orbital theory? How is the bond order determined from molecular orbital theory different from the bond order obtained using Lewis electron structures? How is it similar?
9. What is the effect of placing an electron in an antibonding orbital on the bond order, the stability of the molecule, and the reactivity of a molecule?
10. How can the molecular orbital approach to bonding be used to predict a molecule's stability? What advantages does this method have over the Lewis electron-pair approach to bonding?
11. What is the relationship between bond length and bond order? What effect do antibonding electrons have on bond length? on bond strength?
12. Draw a diagram that illustrates how atomic *p* orbitals can form both σ and π molecular orbitals. Which type of molecular orbital typically results in a stronger bond?
13. What is the minimum number of nodes in σ, π, σ*, and π*? How are the nodes in bonding orbitals different from the nodes in antibonding orbitals?
14. It is possible to form both σ and π molecular orbitals with the overlap of a *d* orbital with a *p* orbital, yet it is possible to form only σ molecular orbitals between *s* and *d* orbitals. Illustrate why this is so with a diagram showing the three types of overlap between this set of orbitals. Include a fourth image that shows why *s* and *d* orbitals cannot combine to form a π molecular orbital.
15. Is it possible for an $np_x$ orbital on one atom to interact with an $np_y$ orbital on another atom to produce molecular orbitals? Why or why not? Can the same be said of $np_y$ and $np_z$ orbitals on adjacent atoms?
16. What is meant by *degenerate orbitals* in molecular orbital theory? Is it possible for σ molecular orbitals to form a degenerate pair? Explain your answer.
17. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals? Why are antibonding molecular orbitals higher in energy than the parent atomic orbitals?
18. What is meant by the *law of conservation of orbitals*?
19. Atomic orbitals on different atoms have different energies. When atomic orbitals from nonidentical atoms are combined to form molecular orbitals, what is the effect of this difference in energy on the resulting molecular orbitals?
20. If two atomic orbitals have different energies, how does this affect the orbital overlap and the molecular orbitals formed by combining the atomic orbitals?
21. Are the Al–Cl bonds in $AlCl_3$ stronger, the same strength, or weaker than the Al–Br bonds in $AlBr_3$? Why?
22. Are the Ga–Cl bonds in $GaCl_3$ stronger, the same strength, or weaker than the Sb–Cl bonds in $SbCl_3$? Why?
23. What is meant by a *nonbonding* molecular orbital, and how is it formed? How does the energy of a nonbonding orbital compare with the energy of bonding or antibonding molecular orbitals derived from the same atomic orbitals?
24. Many features of molecular orbital theory have analogs in Lewis electron structures. How do Lewis electron structures represent
    1. nonbonding electrons?
    2. electrons in bonding molecular orbitals?
25. How does electron screening affect the energy difference between the 2*s* and 2*p* atomic orbitals of the period 2 elements? How does the energy difference between the 2*s* and 2*p* atomic orbitals depend on the effective nuclear charge?
26. For σ versus π, π versus σ*, and σ* versus π*, which of the resulting molecular orbitals is lower in energy?
27. The energy of a σ molecular orbital is usually lower than the energy of a π molecular orbital derived from the same set of atomic orbitals. Under specific conditions, however, the order can be reversed. What causes this reversal? In which portion of the periodic table is this kind of orbital energy reversal most likely to be observed?
28. Is the $\sigma_{2p_z}$ molecular orbital stabilized or destabilized by interaction with the $\sigma_{2s}$ molecular orbital in $N_2$? in $O_2$? In which molecule is this interaction most important?
29. Explain how the Lewis electron-pair approach and molecular orbital theory differ in their treatment of bonding in $O_2$.
30. Why is it crucial to our existence that $O_2$ is paramagnetic?
31. Will NO or CO react more quickly with $O_2$? Explain your answer.
32. How is the energy-level diagram of a heteronuclear diatomic molecule, such as CO, different from that of a homonuclear diatomic molecule, such as $N_2$?

33. How does molecular orbital theory describe the existence of polar bonds? How is this apparent in the molecular orbital diagram of HCl?

## Answers

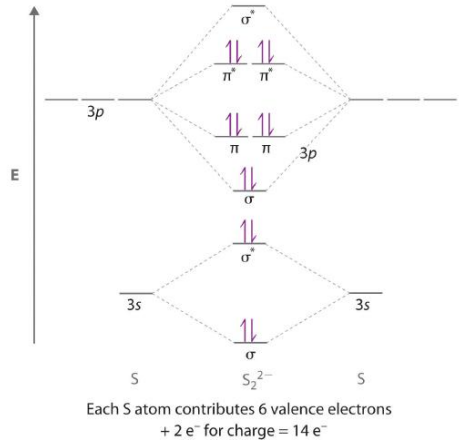
1. An atomic orbital is a region of space around an atom that has a non-zero probability for an electron with a particular energy. Analogously, a molecular orbital is a region of space in a molecule that has a non-zero probability for an electron with a particular energy. Both an atomic orbital and a molecular orbital can contain two electrons.
2.
3.
4.
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8.
9.
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11.
12.
13.
14.
15. No. Because an $np_x$ orbital on one atom is perpendicular to an $np_y$ orbital on an adjacent atom, the net overlap between the two is zero. This is also true for $np_y$ and $np_z$ orbitals on adjacent atoms.
16.
17.
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31.
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33.

## Numerical Problems

1. Use a qualitative molecular orbital energy-level diagram to describe the bonding in $S_2^{2-}$. What is the bond order? How many unpaired electrons does it have?
2. Use a qualitative molecular orbital energy-level diagram to describe the bonding in $F_2^{2+}$. What is the bond order? How many unpaired electrons does it have?
3. If three atomic orbitals combine to form molecular orbitals, how many molecular orbitals are generated? How many molecular orbitals result from the combination of four atomic orbitals? From five?
4. If two atoms interact to form a bond, and each atom has four atomic orbitals, how many molecular orbitals will form?
5. Sketch the possible ways of combining two 1*s* orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.
6. Sketch the *four* possible ways of combining two 2*p* orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.

7. If a diatomic molecule has a bond order of 2 and six bonding electrons, how many antibonding electrons must it have? What would be the corresponding Lewis electron structure (disregarding lone pairs)? What would be the effect of a one-electron reduction on the bond distance?
8. What is the bond order of a diatomic molecule with six bonding electrons and no antibonding electrons? If an analogous diatomic molecule has six bonding electrons and four antibonding electrons, which has the stronger bond? the shorter bond distance? If the highest occupied molecular orbital in both molecules is bonding, how will a one-electron oxidation affect the bond length?
9. Qualitatively discuss how the bond distance in a diatomic molecule would be affected by adding an electron to
    1. an antibonding orbital.
    2. a bonding orbital.
10. Explain why the oxidation of $O_2$ decreases the bond distance, whereas the oxidation of $N_2$ *increases* the N–N distance. Could Lewis electron structures be employed to answer this problem?
11. Draw a molecular orbital energy-level diagram for $Na_2^+$. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will $Na_2^+$, $Na_2$, or $Na_2^-$ be the most stable? Why?
12. Draw a molecular orbital energy-level diagram for $Xe_2^+$, showing only the valence orbitals and electrons. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will $Xe_2^{2+}$, $Xe_2^+$, or $Xe_2$ be most stable? Why?
13. Draw a molecular orbital energy-level diagram for $O_2^{2-}$ and predict its valence electron configuration, bond order, and stability.
14. Draw a molecular orbital energy-level diagram for $C_2^{2-}$ and predict its valence electron configuration, bond order, and stability.
15. If all the *p* orbitals in the valence shells of two atoms interact, how many molecular orbitals are formed? Why is it not possible to form three π orbitals (and the corresponding antibonding orbitals) from the set of six *p* orbitals?
16. Draw a complete energy-level diagram for $B_2$. Determine the bond order and whether the molecule is paramagnetic or diamagnetic. Explain your rationale for the order of the molecular orbitals.
17. Sketch a molecular orbital energy-level diagram for each ion. Based on your diagram, what is the bond order of each species?
    1. $NO^+$
    2. $NO^-$
18. The diatomic molecule BN has never been detected. Assume that its molecular orbital diagram would be similar to that shown for $CN^-$ in Section 5.3 but that the <( \sigma _{2p_{z}} \) molecular orbital is higher in energy than the $\pi_{2p_{x,y}}$ molecular orbitals.
    1. Sketch a molecular orbital diagram for BN.
    2. Based on your diagram, what would be the bond order of this molecule?
    3. Would you expect BN to be stable? Why or why not?
19. Of the species BN, CO, $C_2$, and $N_2$, which are isoelectronic?
20. Of the species $CN^-$, $NO^+$, $B_2^{2-}$, and $O_2^+$, which are isoelectronic?

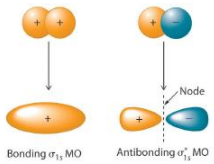
## Answers

1. 

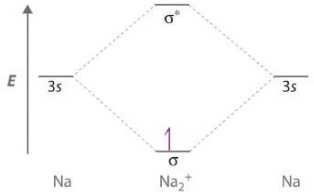
Each S atom contributes 6 valence electrons + 2 e⁻ for charge = 14 e⁻

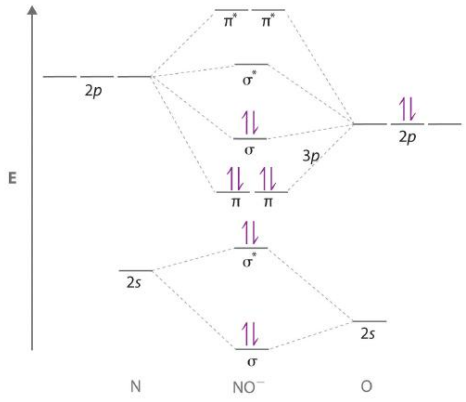
   The bond order is 1, and the ion has no unpaired electrons.

2.

3. The number of molecular orbitals is always equal to the number of atomic orbitals you start with. Thus, combining three atomic orbitals gives three molecular orbitals, and combining four or five atomic orbitals will give four or five molecular orbitals, respectively.
4. 
5. 


   Combining two atomic *s* orbitals gives two molecular orbitals, a σ (bonding) orbital with no nodal planes, and a σ* (antibonding) orbital with a nodal plane perpendicular to the internuclear axis.
6. 
7. 
8. 
9. 1. Adding an electron to an antibonding molecular orbital will decrease the bond order, thereby increasing the bond distance.
   2. Adding an electron to a bonding molecular orbital will increase the bond order, thereby decreasing the bond distance.
10. 
11. Sodium contains only a single valence electron in its 3*s* atomic orbital. Combining two 3*s* atomic orbitals gives two molecular orbitals; as shown in the diagram, these are a σ (bonding) orbital and a σ* (antibonding) orbital.




   Although each sodium atom contributes one valence electron, the +1 charge indicates that one electron has been removed. Placing the single electron in the lowest energy molecular orbital gives a $\sigma_{3s}^1$ electronic configuration and a bond order of 0.5. Consequently, $Na_2^+$ should be a stable species. Oxidizing $Na_2^+$ by one electron to give $Na_2^{2+}$ would remove the electron in the $\sigma_{3s}$ molecular orbital, giving a bond order of 0. Conversely, reducing $Na_2^+$ by one electron to give $Na_2$ would put an additional electron into the $\sigma_{3s}$ molecular orbital, giving a bond order of 1. Thus, reduction to $Na_2$ would produce a more stable species than oxidation to $Na_2^{2+}$. The $Na_2^-$ ion would have two electrons in the bonding $\sigma_{3s}$ molecular orbital and one electron in the $\sigma_{3s}$* antibonding molecular orbital, giving a bond order of 0.5. Thus, $Na_2$ is the most stable of the three species.
12. 
13. 
14. 
15. 
16. 
17. 


    1. The $NO^+$ ion has 10 valence electrons, which fill all the molecular orbitals up to and including the $\sigma_{2p}$. With eight electrons in bonding molecular orbitals and two electrons in antibonding orbitals, the bond order in $NO^+$ is (8 − 2)/2 = 3.
    2. The $NO^-$ ion contains two more electrons, which fill the $\sigma_{2p}^*$ molecular orbital. The bond order in $NO^-$ is (8 − 4)/2 = 2.

18.

19. BN and $C_2$ are isoelectronic, with 12 valence electrons, while $N_2$ and CO are isoelectronic, with 14 valence electrons.

20.

## Contributors

- Anonymous

Modified by Joshua Halpern

Paramagnetism of $O_2$ Video by Harvard Natural Sciences Lecture Demos on YouTube

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# 9.5: Polyatomic Systems, Multiple Bonds, Resonance

**Learning Objectives**

- To explain resonance structures using molecular orbitals.

So far in our molecular orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using molecular orbitals formed by unhybridized *np* atomic orbitals.

## Multiple Bonds

We begin our discussion by considering the bonding in ethylene ($C_2H_4$). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are $sp^2$ hybridized, which means that a singly occupied $sp^2$ orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied $sp^2$ lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H ($sp^2$ + *s*) and one C–C ($sp^2$ + $sp^2$) (part (a) in Figure 6.6.1 ). The $sp^2$ hybridization can be represented as follows:

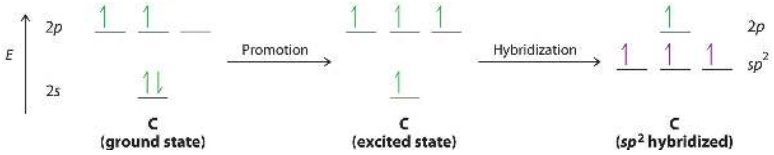
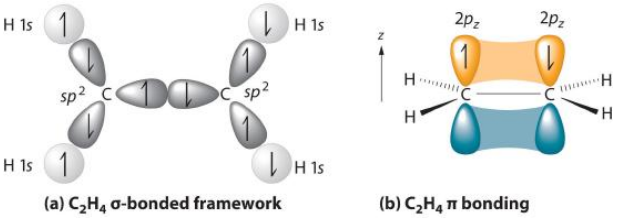


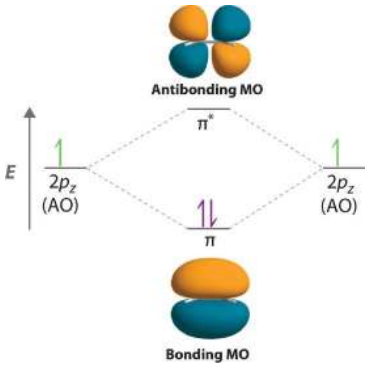

**Figure 6.6.1 Bonding in Ethylene**




*(a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon $sp^2$ hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z-axis.)*

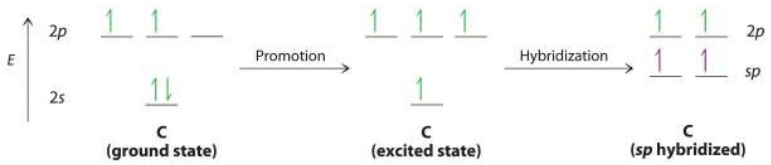
After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 6.6.1 ). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π* antibonding orbital, which produces the energy-level diagram shown in Figure 6.5.2 With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two $CH_2$ fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

**Figure 6.6.2 Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene**



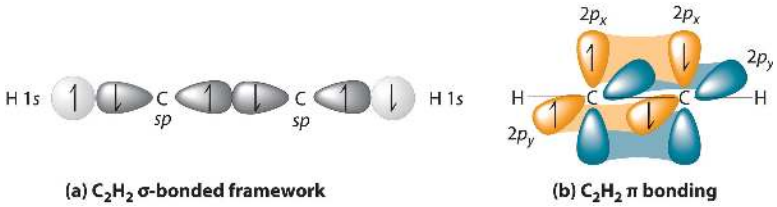

As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbital in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene ($C_2H_2$), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 6.6.4 ).




The two 2*p* orbitals on each carbon can align with the corresponding 2*p* orbitals on the adjacent carbon to simultaneously form a *pair* of π bonds (part (b) in Figure 6.6.4 ). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

**Figure 6.6.4 Bonding in Acetylene**




(a) In the formation of the σ-bonded framework, two sets of singly occupied carbon *sp* hybrid orbitals and two singly occupied hydrogen 1*s* orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

### Note the Pattern

In complex molecules, hybrid orbitals and valence bond theory can be used to describe σ bonding, and unhybridized *π* orbitals and molecular orbital theory can be used to describe π bonding.

### Example 14

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

**Given:** chemical compound and molecular geometry

**Asked for:** bonding description using hybrid atomic orbitals and molecular orbitals

**Strategy:**

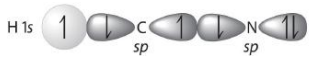
**A** From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

**B** Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π* orbitals.

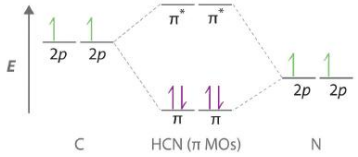
**C** Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

**Solution:**

**A** Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:




**B** We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.




Exercise

Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

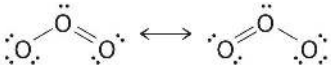
**Answer**

σ-bonding framework: Carbon and oxygen are $sp^2$ hybridized. Two $sp^2$ hybrid orbitals on oxygen have lone pairs, two $sp^2$ hybrid orbitals on carbon form C–H bonds, and one $sp^2$ hybrid orbital on C and O forms a C–O σ bond.

π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

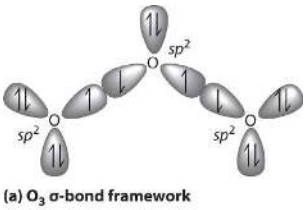
## Molecular Orbitals and Resonance Structures

In Chapter 5 , we used resonance structures to describe the bonding in molecules such as ozone ($O_3$) and the nitrite ion ($NO_2^-$). We showed that ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

**Figure 5.4.5 Bonding in Ozone**



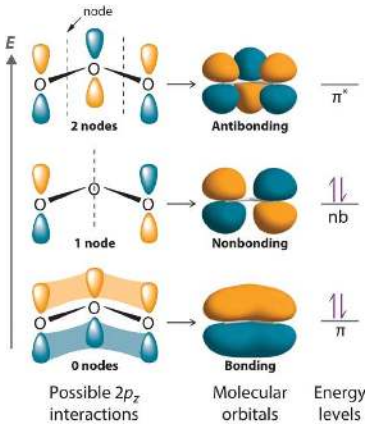

*(a) In the formation of the σ-bonded framework, three sets of oxygen $sp^2$ hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of $O_3$. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons*

.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and $sp^2$ hybridized. If we assume that the terminal oxygen atoms are also $sp^2$ hybridized, then we obtain the σ-bonded framework shown in Figure6.6.5 . Two of the three $sp^2$ lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in $sp^2$ lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so $O_3$ has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.

With a molecular orbital approach to describe the π bonding, three 2*p* atomic orbitals give us three molecular orbitals, as shown in Figure 6.6.6 . One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the $O_3$ plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the $O_3$ plane and passes through the central O atom; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

**Figure 6.6.6 π Bonding in Ozone**




*The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this*

*diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is 1/2 per O–O bond. The combined σ/π bond order is thus 1 1/2 for each O-O bond....*

We can now place the remaining four electrons in the three energy levels shown in Figure 6.6.6 , thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding *three* oxygen atoms together, or 1/2 π bonds per O–O. We therefore predict the overall O–O bond order to be 1 1/2 (1/2 π bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the π nonbonding orbital is localized on the *terminal* O atoms, which suggests that they are more electron rich than the central O atom. The reactivity of ozone is consistent with the predicted charge localization.

### Note the Pattern

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

### Example 15

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the $NO_2^-$ ion is bent.

**Given:** chemical species and molecular geometry

**Asked for:** bonding description using hybrid atomic orbitals and molecular orbitals

**Strategy:**

**A** Calculate the number of valence electrons in $NO_2^-$. From the structure, predict the type of atomic orbital hybridization in the ion.

**B** Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

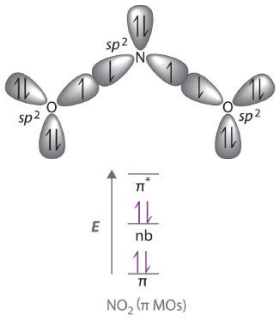
**C** If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

**Solution:**

**A** The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in $NO_2^-$ is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the −1 charge). The bent structure implies that the nitrogen is $sp^2$ hybridized.

**B** If we assume that the oxygen atoms are $sp^2$ hybridized as well, then we can use two $sp^2$ hybrid orbitals on each oxygen and one $sp^2$ hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two $sp^2$ hybrid orbitals on nitrogen form σ bonds with the remaining $sp^2$ hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2*p* orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three 2*p* orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.

**C** Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is 1 1/2 consistent with a resonance structure.




Exercise

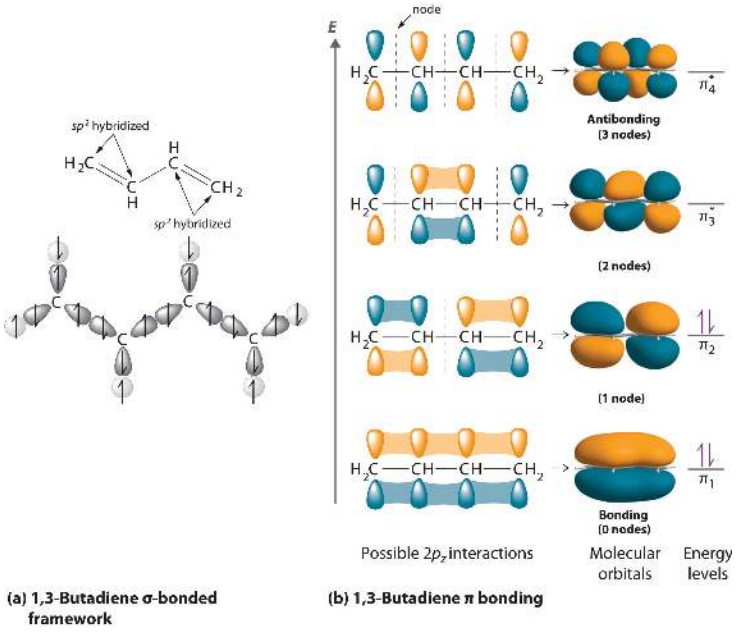
Describe the bonding in the formate ion ($HCO_2^-$), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

**Answer:** Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of $sp^2$ hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized 2*p* orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore 1 1/2

## The Chemistry of Vision

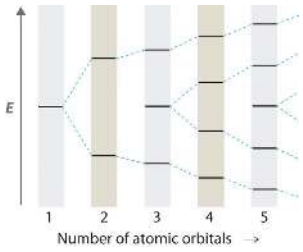
Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 6.6.7. As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 6.6.8 ). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

**Figure 6.6.7 π Bonding in 1,3-Butadiene**




*(a) If each carbon atom is assumed to be $sp^2$ hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving four singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form four molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.*

**Figure 6.6.8 Molecular Orbital Energy-Level Diagrams for a Chain of *n* Like Orbitals That Interact ($n \leq 5$)**




*As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.*

### Note the Pattern

As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

### Summary

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as $O_2$ and $N_2$. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

### Key Takeaway

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

### Conceptual Problems

1. What information is obtained by using the molecular orbital approach to bonding in $O_3$ that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?
2. How is resonance explained using the molecular orbital approach?
3. Indicate what information can be obtained by each method:

| | Lewis Electron Structures | VSEPR Model | Valence Bond Theory | Molecular Orbital Theory |
|---|---|---|---|---|
| Geometry | | | | |
| Resonance | | | | |
| Orbital Hybridization | | | | |
| Reactivity | | | | |
| Expanded Valences | | | | |
| Bond Order | | | | |

## Numerical Problems

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in $BCl_3$ and $CS_3^{2-}$.
2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in $CO_2$ and $N_3^-$.

## Contributors

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Modified by Joshua Halpern

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# CHAPTER OVERVIEW

## 10: Gases


10.1: Gaseous Elements and Compounds
10.2: Gas Pressure
10.3: The Ideal Gas Law
10.4: The Combined Gas Law
10.5: Gas Mixtures
10.6: Stoichiometry Involving Gases
10.7: The Kinetic Theory of Gases
10.8: Real Gases
10.9: Essential Skills 5


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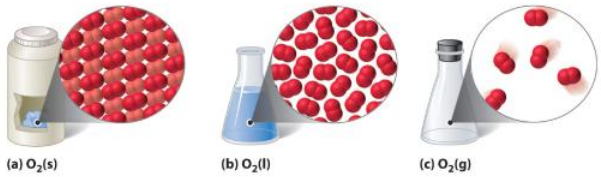
# 10.1: Gaseous Elements and Compounds

**Learning Objectives**

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 10.1.1 compares the three states of matter and illustrates the differences at the molecular level.

**Figure 10.1.1 A Diatomic Substance ($O_2$) in the Solid, Liquid, and Gaseous States**




(a) Solid $O_2$ has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid $O_2$ conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous $O_2$ fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, $H_2O$ is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vaporThe distinction between a gas and a vapor is subtle: the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions (25°C, 1.0 atm). Nitrogen ($N_2$) and oxygen ($O_2$) are thus referred to as gases, but gaseous water in the atmosphere is called water vapor. is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 10.1.1

**Table 10.1.1 Properties of Water at 1.0 atm**

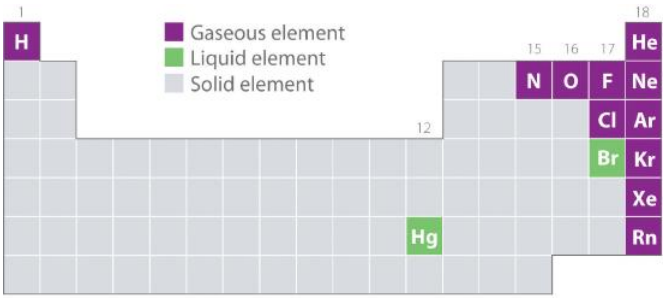
| Temperature | State | Density ($g/cm^3$) |
|---|---|---|
| ≤0°C | solid (ice) | 0.9167 (at 0.0°C) |
| 0°C–100°C | liquid (water) | 0.9997 (at 4.0°C) |
| ≥100°C | vapor (steam) | 0.005476 (at 127°C) |

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 10.1.2 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules ($H_2$, $N_2$, $O_2$, $F_2$, and $Cl_2$).

Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone ($O_3$), which is also a gas. In contrast, bromine (as $Br_2$) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

**Figure 10.1.2 Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm**




*The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.*

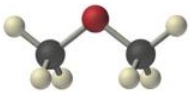
Many of the elements and compounds we have encountered so far are typically found as gases; some of the more common ones are listed in Table 10.1.2 . Gaseous substances include many binary hydrides, such as the hydrogen halides (HX); hydrides of the chalcogens; hydrides of the group 15 elements N, P, and As; hydrides of the group 14 elements C, Si, and Ge; and diborane ($B_2H_6$). In addition, many of the simple covalent oxides of the nonmetals are gases, such as CO, $CO_2$, NO, $NO_2$, $SO_2$, $SO_3$, and $ClO_2$. Many low-molecular-mass organic compounds are gases as well, including all the hydrocarbons with four or fewer carbon atoms and simple molecules such as dimethyl ether [$(CH_3)_2O$], methyl chloride ($CH_3Cl$), formaldehyde ($CH_2O$), and acetaldehyde ($CH_3CHO$). Finally, refrigerants, such as the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs) are gases which can be easily liquified by compression and in turn the liquids can be turned into gases by decreasing the pressure on the liquids. The phase change from liquid to gas in tubes inside the refrigerator cools, while the compression in coils at the bottom or back of the refrigerator warms the room. Ammonia and $SO_2$ are other compressible gases that have been used as refrigerants but cannot be used in houses because of their poisonous nature. Ammonia is still used as a refrigerant in large commercial settings because of its efficiency and low cost.

**Table 10.1.2 Some Common Substances That Are Gases at 25°C and 1.0 atm**

| Elements | Compounds | |
|---|---|---|
| He (helium) | HF (hydrogen fluoride) | $C_2H_4$ (ethylene) |
| Ne (neon) | HCl (hydrogen chloride) | $C_2H_2$ (acetylene) |
| Ar (argon) | HBr (hydrogen bromide) | $C_3H_8$ (propane) |
| Kr (krypton) | HI (hydrogen iodide) | $C_4H_{10}$ (butane) |
| Xe (xenon) | HCN (hydrogen cyanide)* | CO (carbon monoxide) |
| Rn (radon) | $H_2S$ (hydrogen sulfide) | $CO_2$ (carbon dioxide) |
| $H_2$ (hydrogen) | $NH_3$ (ammonia) | NO (nitric oxide) |
| $N_2$ (nitrogen) | $PH_3$ (phosphine) | $N_2O$ (nitrous oxide) |
| $O_2$ (oxygen) | $CH_4$ (methane) | $NO_2$ (nitrogen dioxide) |
| $O_3$ (ozone) | $C_2H_6$ (ethane) | $SO_2$ (sulfur dioxide) |
| $F_2$ (fluorine) | | |
| $Cl_2$ (chlorine) | | |

*HCN boils at 26°C at 1 atm, so it is included in this table.

All of the gaseous substances mentioned previously (other than the monatomic noble gases) contain covalent or polar covalent bonds and are nonpolar or polar molecules. In contrast, the strong electrostatic attractions in ionic compounds, such as NaBr (boiling point = 1390°C) or LiF (boiling point = 1673°C), prevent them from existing as gases at room temperature and pressure. In addition, the lightest members of any given family of compounds are most likely gases, and the boiling points of polar compounds are generally greater than those of nonpolar compounds of similar molecular mass. Therefore, in a given series of compounds, the lightest and least polar members are the ones most likely to be gases. With relatively few exceptions, however, compounds with more than about five atoms from period 2 or below are too heavy to exist as gases under normal conditions.



Dimethyl ether

## Note the Pattern

Gaseous substances often contain covalent or polar covalent bonds, exist as nonpolar or slightly polar molecules, have relatively low molecular masses, and contain five or fewer atoms from periods 1 or 2.

While gases have a wide array of uses, a particularly grim use of a gaseous substance is believed to have been employed by the Persians on the Roman city of Dura in eastern Syria in the third century AD. The Persians dug a tunnel underneath the city wall to enter and conquer the city. Archeological evidence suggests that when the Romans responded with counter-tunnels to stop the siege, the Persians ignited bitumen and sulfur crystals to produce a dense, poisonous gas. It is likely that bellows or chimneys distributed the toxic fumes. The remains of about 20 Roman soldiers were discovered at the base of the city wall at the entrance to a tunnel that was less than 2 m high and 11 m long. Because it is highly unlikely that the Persians could have slaughtered so many Romans at the entrance to such a confined space, archeologists speculate that the ancient Persians used chemical warfare to successfully conquer the city.

## Example 10.1.1

Which compounds would you predict to be gases at room temperature and pressure?

1. cyclohexene
2. lithium carbonate

3. cyclobutane
4. vanadium(III) oxide
5. benzoic acid ($C_6H_5CO_2H$)

**Given:** compounds

**Asked for:** physical state

**Strategy:**

**A** Decide whether each compound is ionic or covalent. An ionic compound is most likely a solid at room temperature and pressure, whereas a covalent compound may be a solid, a liquid, or a gas.

**B** Among the covalent compounds, those that are relatively nonpolar and have low molecular masses are most likely gases at room temperature and pressure.

**Solution:**

**A** Lithium carbonate is $Li_2CO_3$, containing $Li^+$ and $CO_3^{2-}$ ions, and vanadium(III) oxide is $V_2O_3$, containing $V^{3+}$ and $O^{2-}$ ions. Both are primarily ionic compounds that are expected to be solids. The remaining three compounds are all covalent.

**B** Benzoic acid has more than four carbon atoms and is polar, so it is not likely to be a gas. Both cyclohexene and cyclobutane are essentially nonpolar molecules, but cyclobutane ($C_4H_8$) has a significantly lower molecular mass than cyclohexene ($C_6H_{10}$), which again has more than four carbon atoms. We therefore predict that cyclobutane is most likely a gas at room temperature and pressure, while cyclohexene is a liquid. In fact, with a boiling point of only 12°C, compared to 83°C for cyclohexene, cyclobutane is indeed a gas at room temperature and pressure.

Exercise

Which compounds would you predict to be gases at room temperature and pressure?

1. *n*-butanol
2. ammonium fluoride ($NH_4F$)
3. ClF
4. ethylene oxide



5. $HClO_4$

**Answer:** c; d

## Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, $N_2$, $O_2$). Many inorganic and organic compounds with four or fewer nonhydrogen atoms are also gases at room temperature and pressure. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

## Key Takeaway

- The molecules in gaseous substances often contain covalent or polar covalent bonds, are nonpolar or slightly polar molecules, and have relatively low molecular masses.

## Conceptual Problems

1. Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?
2. Determine whether the melting point, the dipole moment, and electrical conductivity are macroscopic or microscopic properties of matter and explain your reasoning.

3. How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not? Can polarity be related to boiling point?
4. For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing
    1. density.
    2. strength of intermolecular interactions.
    3. compressibility.
    4. molecular motion.
    5. order in the arrangement of the molecules or atoms.
5. Explain what is wrong with this statement: “The state of matter largely determines the molecular properties of a substance.”
6. Describe the most important factors that determine the state of a given compound. What external conditions influence whether a substance exists in any one of the three states of matter?
7. Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?
8. Is the following observation correct? “Almost all nonmetal binary hydrides are gases at room temperature, but metal hydrides are all solids.” Explain your reasoning.
9. Is the following observation correct? “All the hydrides of the chalcogens are gases at room temperature and pressure except the binary hydride of oxygen, which is a liquid.” Explain your reasoning. Would you expect 1-chloropropane to be a gas? iodopropane? Why?
10. Explain why ionic compounds are not gases under normal conditions.

## Answers

1.
2.
3.
4.
5. The molecular properties of a substance control its state of matter under a given set of conditions, *not* the other way around. The presence of strong intermolecular forces favors a condensed state of matter (liquid or solid), while very weak intermolecular interaction favor the gaseous state. In addition, the shape of the molecules dictates whether a condensed phase is a liquid or a solid.
6.
7. Elements that exist as gases are mainly found in the upper right corner and on the right side of the periodic table. The following elements exist as gases: H, He, N, O, F, Ne, Cl, Ar, Kr, Xe, and Rn. Thus, half of the halogens, all of the noble gases, and the lightest chalcogens and picnogens are gases. Of these, all except the noble gases exist as diatomic molecules. Only two elements exist as liquids at a normal room temperature of 20°C–25°C: mercury and bromine. The upper right portion of the periodic table also includes most of the elements whose binary hydrides are gases. In addition, the binary hydrides of the elements of Groups 14–16 are gases.
8.
9.
10.

## Contributors

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Modified by Joshua Halpern

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# 10.2: Gas Pressure

**Learning Objectives**

- To describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities: *temperature* (expressed in kelvins), *volume* (expressed in liters), *amount* (expressed in moles), and *pressure* (in atmospheres). As we explain in this section and Section 10.3, these variables are *not* independent. If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

## Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure(*P*)The amount of force (F)(A)P = F/A of the gas, the force (*F*) per unit area (*A*) of surface:

$$P = \frac{F}{A}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 10.2.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. In the English system, the units of force are pounds and the units of area are square inches, so we often see pressure expressed in pounds per square inch ($lb/in^2$, or psi), particularly among engineers. For scientific measurements, however, the SI units for force are preferred. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter ($N/m^2$), which is called the pascal (Pa)The SI unit for pressure. The pascal is newtons per square meter: $N/m^2$, after the French mathematician Blaise Pascal (1623–1662):

$$1\ Pa = 1\ N/m^2$$

To convert from pounds per square inch to pascals, multiply psi by 6894.757 [1 Pa = 1 psi (6894.757)].

### Blaise Pascal (1623–1662)

In addition to his talents in mathematics (he invented modern probability theory), Pascal did research in physics and was an author and a religious philosopher as well. His accomplishments include invention of the first syringe and the first digital calculator and development of the principle of hydraulic pressure transmission now used in brake systems and hydraulic lifts.

### Example 10.2.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

1. lying flat?
2. standing on edge in a bookcase?

**Given:** mass and dimensions of object

**Asked for:** pressure

**Strategy:**

**A** Calculate the force exerted by the book and then compute the area that is in contact with a surface.

**B** Substitute these two values into Equation 10.2.1 to find the pressure exerted on the surface in each orientation.

**Solution:**

The force exerted by the book does *not* depend on its orientation. Recall from Section 9.1 that the force exerted by an object is $F = ma$, where $m$ is its mass and $a$ is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s$^2$ at Earth's surface). In SI units, the force exerted by the book is therefore

$F = ma$ = (2.00 kg)(9.8067 m/s$^2$) = 19.6 (kg·m)/s$^2$ = 19.6 N

1. **A** We calculated the force as 19.6 N. When the book is lying flat, the area is (0.270 m)(0.210 m) = 0.0567 m$^2$. **B** The pressure exerted by the text lying flat is thus $P = \frac{19.6\ N}{0.0567\ m^2} = 3.46 \times 10^2\ Pa$
2. **A** If the book is standing on its end, the force remains the same, but the area decreases: $(21.0\ cm)\,(4.5\ cm) = (0.210\ m)\,(0.045\ m) = 9.5 \times \times 10^{-3}\ m^2$

   **B** The pressure exerted by the book in this position is thus

   $P = \frac{19.6\ N}{9.5 \times 10^{-3}\ m^2} = 2.1 \times 10^3\ Pa$

   Thus the *pressure* exerted by the book varies by a factor of about six depending on its orientation, although the *force* exerted by the book does not vary.

Exercise

What pressure does a 60.0 kg student exert on the floor

1. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm$^2$)?
2. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm$^2$)?

**Answers:**

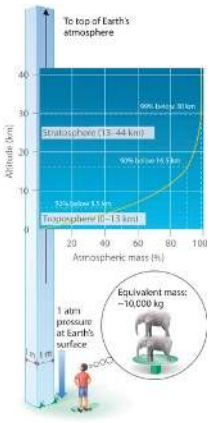
1. 3.27 × 10$^4$ Pa (4.74 lb/in.$^2$)
2. 5.9 × 10$^6$ Pa (8.5 × 10$^2$ lb/in.$^2$)

## Atmospheric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface, and half of it is within the first 5.5 km (Figure 9.3). Every point on Earth's surface experiences a net pressure called *atmospheric pressure*. The pressure exerted by the atmosphere is considerable: a 1.0 m$^2$ column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 100 kPa:

$$Pressure = \frac{(1.0 \times 10^4\ kg)\,(9,807\ \cancel{m}/s^2)}{1.0\ \cancel{m^2}} = 0.98 \times 10^5\ Pa = 98\ kPa$$

**Figure 10.2.1 Atmospheric Pressure**



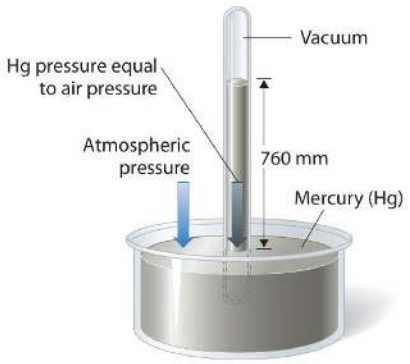

*Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface, resulting in a pressure at the surface of 1.01 × 10$^5$ N/m$^2$. This corresponds to a pressure of 101 kPa = 760 mmHg*

= *1 atm.*

In English units, this is about 14 lb/in.$^2$, but we are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of atmospheric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The atmospheric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Atmospheric pressure can be measured using a barometerA device used to measure atmospheric pressure., a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 10.2.1). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a *vacuum*), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 10.2.2 This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

**Figure 10.2.2 A Mercury Barometer**




*The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.*

Mercury barometers have been used to measure atmospheric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg)A unit of pressure, often called the torr., often called the torrA unit of pressure. One torr is the same as 1 mmHg., after Torricelli. Standard atmospheric pressureThe atmospheric pressure required to support a column of mercury exactly 760 mm tall, which is also referred to as 1 atmosphere (atm). is the atmospheric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm)Also referred to as standard atmospheric pressure, it is the atmospheric pressure required to support a column of mercury exactly 760 mm tall.. These units are also related to the pascal:

$$1\ atm = 760\ mmHg = 760\ torr = 1.01325 \times \times 10^5\ Pa = 101.325\ kPa$$

Thus a pressure of 1 atm equals 760 mmHg exactly and is approximately equal to 100 kPa.

While mercury barometers were the workhorses for pressure measurement into the last quarter of the 20th century, they have been replaced by electronic gauges. One motivation was safety. Mercury and mercury vapor are heavy metal poisons.

The oldest and simplest replacement for mercury barometers are aneroid gauges. The simplest version of an aneroid gauge (Figure 6.2.3) has a thin metal diaphram which expands and contracts. The diaphragm is connected to a dial by a mechanical linkage.

Aneroid gauges can either be absolute or differential. Differential aneroid gauges compare the pressure in the gauge housing to that being measured. A common use for aneroid gauges was airplane altimeters.

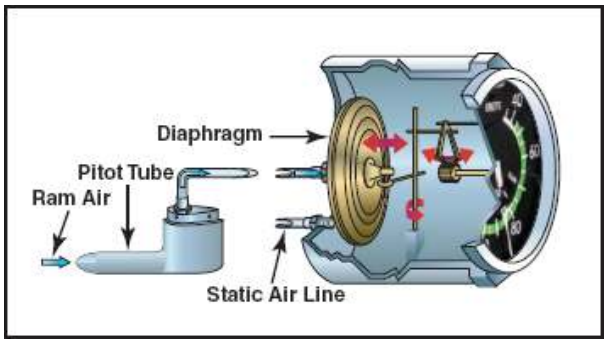



Figure 6.2.2 An Aneroid Barometer *An Aneroid Barometer uses the expansion/contraction of a metal diaphragm to move the indicator dial. This drawing from the Wikipedia shows a simple aneroid barometer used for an airplane altimeter.*

Most modern pressure sensors are based on strain gauge which convert pressure into a strain on a semiconductor element. The strain is converted into an electrical signal by the piezoelectric effect as a change in resistance monitored by a resistance bridge. Alternatively pressure is related to the change in frequency of a quartz crystal oscillator. Modern balances are also based on this later principle.

A very accurate type of pressure sensor uses a metal diaphragm as one part of a capacitor. As the pressure changes the diaphragm moves altering the capacitance. Handbooks are available from sensor manufacturers with details including OMEGA and WIKA.

Below atmospheric pressures another type of gauge is used based on measuring temperature change of a hot wire as a function of pressure. This is best suited to pressures below atmospheric. Older types called thermocouple or Pirani gauges measure only up to a few Torr. Modern variations called convection gauges can measure up to atmospheric pressure

A summary of the various types of pressure gauge in use today can be found in a technical note at the Kurt Lesker site

Pressure gauges specify whether the measurement is absolute (relative to zero pressure) or gauge (relative to the standard atmosphere). One must be careful about which kind a gauge is when buying or using one..

### Example 10.2.2

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the atmospheric pressure is only 454 mmHg. Convert this pressure to

1. atmospheres.
2. kilopascals.

**Given:** pressure in millimeters of mercury

**Asked for:** pressure in atmospheres and kilopascals

**Strategy:**

Use the conversion factors in Equation 10.2.4 to convert from millimeters of mercury to atmospheres and kilopascals.

**Solution:**

From Equation 10.2,4, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = \left(454 \ \cancel{mmHg}\right)\left(\frac{1 \ atm}{760 \ \cancel{mmHg}}\right) = 0.597 \ atm$$

The pressure in kPa is given by

$$P = \left(0.597 \ \cancel{atm}\right)\left(\frac{101.325 \ kPa}{1 \ \cancel{atm}}\right) = 80.5 \ kPa$$

Exercise

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal atmospheric pressure at this altitude is about 0.308 atm. Convert this pressure to

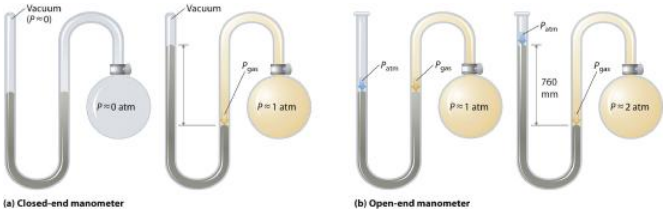
1. millimeters of mercury.
2. kilopascals.

**Answer:** a. 234 mmHg; b. 31.2 kPa

## Manometers

Barometers measure atmospheric pressure, but manometersA device used to measure the pressures of samples of gases contained in an apparatus. measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 10.2.3. When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

**Figure 10.2.3 The Two Types of Manometer**




*(a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum (P ≈ 0), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere (P ≈ 1 atm), and the difference in the heights of the two columns gives the difference between atmospheric pressure and the pressure of the gas in the bulb.*

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 10.2.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the atmospheric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the atmospheric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the atmospheric pressure minus the difference in the heights of the two columns.

### Example 10.2.3

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (At 25°C, the density of water is 0.9970 g/cm$^3$; the density of mercury is 13.53 g/cm$^3$.)

**Given:** pressure range and densities of water and mercury

**Asked for:** column height

**Strategy:**

**A** Calculate the height of a column of mercury corresponding to 0.200 atm in millimeters of mercury. This is the height needed for a mercury-filled column.

**B** From the given densities, use a proportion to compute the height needed for a water-filled column.

**Solution:**

**A** In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = (0.200\ \cancel{atm}) \left( \frac{760\ mmHg}{1\ \cancel{atm}} \right) = 152\ mmHg$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

**B** Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury ($d_{Hg}$)($d_{H2O}$)

$$(height_{H_2O})\,(d_{H_2O}) = (height_{Hg})\,(d_{Hg})$$

$$height_{H_2O} = (height_{Hg})\,\frac{d_{Hg}}{d_{H_2O}}$$

$$= (152\ mmHg) \left( \frac{13.53\ \cancel{g/cm^2}}{0.9970\ \cancel{g/cm^2}} \right)$$

$$= 2.06 \times 10^3\ mm\ H_2O$$

This answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise

Suppose you want to design a barometer to measure atmospheric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm$^3$. How tall a column of gallium do you need if $P$ = 1.00 atm?

**Answer:** 1.68 m

The answer to Example 4 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. If a column of water 2.06 m high corresponds to 0.200 atm, then 1.00 atm corresponds to a column height of

$$\frac{h}{2.06\ m} = \frac{1.00\ \cancel{atm}}{0.200\ \cancel{atm}}$$

$$h = 10.3\ m$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on atmospheric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for atmospheric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

## Summary

Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m$^2$). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *atmospheric pressure*, is about 101 kPa or 14.7 lb/in.$^2$ at sea level. Atmospheric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to atmospheric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard atmospheric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.

## Key Takeaway

- Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer.

## Key Equation

**Definition of pressure**

Equation 10.2.1: $P = F/A$

## Conceptual Problems

1. What four quantities must be known to completely describe a sample of a gas? What units are commonly used for each quantity?
2. If the applied force is constant, how does the pressure exerted by an object change as the area on which the force is exerted decreases? In the real world, how does this relationship apply to the ease of driving a small nail versus a large nail?
3. As the force on a fixed area increases, does the pressure increase or decrease? With this in mind, would you expect a heavy person to need smaller or larger snowshoes than a lighter person? Explain.
4. What do we mean by *atmospheric pressure*? Is the atmospheric pressure at the summit of Mt. Rainier greater than or less than the pressure in Miami, Florida? Why?
5. Which has the highest atmospheric pressure—a cave in the Himalayas, a mine in South Africa, or a beach house in Florida? Which has the lowest?
6. Mars has an average atmospheric pressure of 0.007 atm. Would it be easier or harder to drink liquid from a straw on Mars than on Earth? Explain your answer.
7. Is the pressure exerted by a 1.0 kg mass on a 2.0 $m^2$ area greater than or less than the pressure exerted by a 1.0 kg mass on a 1.0 $m^2$ area? What is the difference, if any, between the pressure of the atmosphere exerted on a 1.0 $m^2$ piston and a 2.0 $m^2$ piston?
8. If you used water in a barometer instead of mercury, what would be the major difference in the instrument?

## Answer

1.
2.
3. Because pressure is defined as the force per unit area ($P = F/A$), increasing the force on a given area increases the pressure. A heavy person requires larger snowshoes than a lighter person. Spreading the force exerted on the heavier person by gravity (that is, their weight) over a larger area decreases the pressure exerted per unit of area, such as a square inch, and makes them less likely to sink into the snow.
4.
5.
6.
7.
8.

## Numerical Problems

1. Calculate the pressure in atmospheres and kilopascals exerted by a fish tank that is 2.0 ft long, 1.0 ft wide, and 2.5 ft high and contains 25.0 gal of water in a room that is at 20°C; the tank itself weighs 15 lb ($d_{H_2O}$= 1.00 g/$cm^3$ at 20°C). If the tank were 1 ft long, 1 ft wide, and 5 ft high, would it exert the same pressure? Explain your answer.
2. Calculate the pressure in pascals and in atmospheres exerted by a carton of milk that weighs 1.5 kg and has a base of 7.0 cm × 7.0 cm. If the carton were lying on its side (height = 25 cm), would it exert more or less pressure? Explain your reasoning.
3. If atmospheric pressure at sea level is $1.0 \times 10^5$ Pa, what is the mass of air in kilograms above a 1.0 $cm^2$ area of your skin as you lie on the beach? If atmospheric pressure is $8.2 \times 10^4$ Pa on a mountaintop, what is the mass of air in kilograms above a 4.0 $cm^2$ patch of skin?
4. Complete the following table:

| atm | kPa | mmHg | torr |
|---|---|---|---|
| 1.40 | | | |
| | | 723 | |
| | 43.2 | | |

5. The SI unit of pressure is the pascal, which is equal to 1 $N/m^2$. Show how the product of the mass of an object and the acceleration due to gravity result in a force that, when exerted on a given area, leads to a pressure in the correct SI units. What mass in kilograms applied to a 1.0 $cm^2$ area is required to produce a pressure of
    1. 1.0 atm?
    2. 1.0 torr?
    3. 1 mmHg?
    4. 1 kPa?
6. If you constructed a manometer to measure gas pressures over the range 0.60–1.40 atm using the liquids given in the following table, how tall a column would you need for each liquid? The density of mercury is 13.5 $g/cm^3$. Based on your results, explain why mercury is still used in barometers, despite its toxicity.

| | Liquid Density (20°C) | Column Height (m) |
|---|---|---|
| isopropanol | 0.785 | |
| coconut oil | 0.924 | |
| glycerine | 1.259 | |

## Answer

1. 5.4 kPa or $5.3 \times 10^{-2}$ atm; 11 kPa, $1.1 \times 10^{-3}$ atm; the same force acting on a smaller area results in a greater pressure.
2. 
3. 
4. 
5. 
6. 

## Contributors

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Modified by Joshua Halpern

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# 10.3: The Ideal Gas Law

**Learning Objectives**

- To use the ideal gas law to describe the behavior of a gas.

In a gas, molecules freely move, filling any volume that they occupy. The kinetic energy of the molecules greatly exceeds any potential energy of attraction or repulsion between molecules and the size of the molecules are miniscule compared to the average space between them. Contrast this with solids, where the molecules are held in place by the attractive forces and the comparatively small kinetic energy only results in the molecules jiggling in place when thermally excited. Again, in a solid, the molecules are packed so closely together that the volume of the solid is essentially that of the sum of the molecular volumes of all of the molecules in it. Liquids represent a situation where molecular attraction and kinetic energy are balanced and the spacing between molecules is higher than in solids but much less than in gases.

At high temperatures and low pressures, where the kinetic energy and the spacing between molecules are both large, one may neglect both the miniscule attractive forces and molecular volume. Under such conditions the properties of the gas, the pressure, P, volume, V, number of moles, n, and the temperature, T are independent of the mixture of molecules in the gas. In that limit the behavior of the gas is called ideal, and governed by the ideal gas law

No gases are truly ideal, but while no model is perfect, some are useful, and under most commonly encountered conditions, the ideal gas law is very useful indeed to describe the behavior of gases. It is also easy to predict that the conditions where the ideal gas law would have trouble describing the behavior of a gas would be low temperature (small molecular kinetic energy) and high pressure (little space between molecules). The behavior of gases under such conditions becomes increasingly like that of liquids and will be discussed in the next chapter.

## The Ideal Gas Law

The ideal gas law

$$PV = nRT$$

relates the pressure, volume, temperature and number of moles in a gas to each other. R is a constant called the gas constant. The ideal gas law is what is called an equation of state because it is a complete description of the gas's thermodynamic state. No other information is needed to calculate any other thermodynamic variable, and, since the equation relates four variables, a knowledge of any three of them is sufficient.

Pressure, volume and number of moles, the latter sometime called extent, share an important property, they can never be negative. What would a negative volume be, or an absolute negative pressure or extent? The concepts do not even exist. This means that temperature in the ideal gas law is similarly limited. **It can never be negative.**

We can determine what zero temperature on the ideal gas scale is by holding the number of moles and the pressure constant and extrapolate the temperature measured in Celcius to what its value would be at zero volume

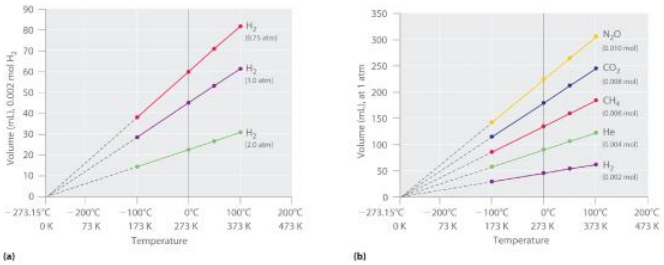



Figure 10.3.1 *The Relationship between Volume and Temperature (a) In these plots of volume versus temperature for equal-sized samples of $H_2$ at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to V = 0. The temperature scale is given in both degrees Celsius and Kelvin. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at V = 0 (−273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of V = 0 at −273.15°C, regardless of the identity or the amount of the gas.*

The extrapolated temperature corresponding to zero volume at constant pressure and amount is -273.15 °C, which is called absolute zero because no lower temperature is possible (unless, of course you can come up with a negative volumes, but you cannot). For convenience we set the degrees on the Kelvin scale to the size of the degree on the Celcius scale. In other words

$1\ K = 1^oC$

### Note the Pattern

Before we can use the ideal gas law, however, we need to know the value of the gas constant *R*. Its form depends on the units used for the other quantities in the expression. If *V* is expressed in liters (L), *P* in atmospheres (atm), *T* in kelvins (K), and *n* in moles (mol), then

$R = 0.08206\ L \cdot atm/\left(K \cdot \cdot mol\right)$

Because the product *PV* has the units of energy, as described in Section 8.1 and Essential Skills 4 (Section 9.9), *R* can also have units of J/(K·mol) or cal/(K·mol):

$R = 8.3145\ J/\left(K \cdot mol\right) = 1.9872 cal/\left(K \cdot mol\right)$

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 atm pressure, referred to as standard temperature and pressure (STP) The conditions 0°C (273.15 K) and 1 atm pressure for a gas.

This can be confusing because as discussed in the previous chapter,the standard state for enthalpies of reaction and formation is 298K. Be sure to use the appropriate standard state for enthalpies (298 K) and gas problems (273.15 K)

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 10.3.1:

$$V = \frac{nRT}{P} = \frac{\left(1.000\ \cancel{mol}\right)\left(0.082057\ L \cdot \cancel{atm}/\cancel{K \cdot mol}\right)\left(273.15\ \cancel{K}\right)}{1.000\ \cancel{atm}} = 22.31\ L$$

Thus the volume of 1 mol of an ideal gas at 0°C and 1 atm pressure is 22.41 L, approximately equivalent to the volume of three basketballs. The quantity 22.41 L is called the standard molar volumeThe volume of 1 mol of an ideal gas at STP (0°C and 1 atm pressure), which is 22.41 L. of an ideal gas. The molar volumes of several real gases at STP are given in Table 10.3.1, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at STP.

**Table 10.3.1** *Molar Volumes of Selected Gases at Standard Temperature (0°C) and Pressure (1 atm)*

| Gas | Molar Volume (L) |
|---|---|
| He | 22.434 |
| Ar | 22.397 |
| $H_2$ | 22.433 |
| $N_2$ | 22.402 |
| $O_2$ | 22.397 |
| $CO_2$ | 22.260 |
| $NH_3$ | 22.079 |

## Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same

equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

### Example 10.3.1

The balloon that Charles used for hisflight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 $ft^3$), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

**Given:** volume, temperature, and pressure

**Asked for:** amount of gas

**Strategy:**

**A** Solve the ideal gas law for the unknown quantity, in this case *n*.

**B** Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

**Solution:**

**A** We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 10.3.1) for *n*, we obtain

$$n = \frac{PV}{RT}$$

**B** *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.082057 (L·atm)/(K·mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$745 \ \cancel{\text{mmHg}} \times \frac{1 \text{ atm}}{760 \ \cancel{\text{mmHg}}} = 0.980 \text{ atm} \tag{10.3.1}$$

$$T = 273 + 30 = 303\text{K} \tag{10.3.2}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980 \ \cancel{\text{atm}} \times 31150 \ \cancel{L}}{0.08206 \frac{\cancel{\text{atm}} \cdot \cancel{L}}{\text{mol} \cdot \cancel{\text{K}}} \times 303 \ \cancel{\text{K}}} = 1.23 \times 10^3 \text{ mol} \tag{10.3.3}$$

Exercise

Suppose that an "empty" aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as $CO_2$. What is the pressure of the gas at 25°C?

**Answer:** 1.5 atm

In Example 5, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 6.

## Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \tag{10.3.6}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (*m*, in grams) divided by its molar mass (*M*, in grams per mole):

$$n = \frac{m}{M} \tag{10.3.7}$$

Substituting this expression for *n* into Equation 10.4.12 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{10.3.8}$$

Because *m*/*V* is the density *d* of a substance, we can replace *m*/*V* by *d* and rearrange to give

$$d = \frac{m}{V} = \frac{MP}{RT} \tag{10.3.9}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

### Example 10.3.2

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

**Given:** compound, temperature, and pressure

**Asked for:** density

**Strategy:**

**A** Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.

**B** Substitute these values into Equation 10.3.9 to obtain the density.

**Solution:**

**A** The molar mass of butane ($C_4H_{10}$) is

\( (4)(12.011) + (10)(1.0079) = 58.123 \; g/mol \notag \)

Using 0.082057 (L·atm)/(K·mol) for *R* means that we need to convert the temperature from degrees Celsius to kelvins (*T* = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm}$$

**B** Substituting these values into Equation 10.3.9 gives

$$d = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L}$$

Exercise

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

**Answer:** radon, 9.23 g/L; $N_2$, 1.17 g/L

A common use of Equation 10.3.9 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and re-weighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 10.

### Example 10.3.3

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

**Given:** pressure, temperature, mass, and volume

**Asked for:** molar mass and chemical formula

**Strategy:**

**A** Solve Equation 10.3.8 for the molar mass of the gas and then calculate the density of the gas from the information given.

**B** Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

**C** Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

**Solution:**

**A** Solving Equation 10.3.8 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P}$$

Density is the mass of the gas divided by its volume:

$$d = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L}$$

**B** We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K$$

$$P = 727\text{mmHg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm}$$

The molar mass of the unknown gas is thus

$$d = \frac{1.84\text{ g/L} \times 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol}$$

**C** The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol}$$

The most likely choice is $NO_2$ which is in agreement with the data. The red-brown color of smog also results from the presence of $NO_2$ gas.

Exercise

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

**Answer:** 44 g/mol; $CO_2$

## Summary

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, $PV = nRT$. The proportionality constant, $R$, is called the **gas constant** and has the value 0.08206 (L·atm)/(K·mol), 8.3145 J/(K·mol), or 1.9872 cal/(K·mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity ($P$, $V$, $T$, or $n$) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of $P$, $V$, $T$, and $n$) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

## Key Takeaway

- The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

## Key Equations

**Ideal gas law**

Equation 10.3.1: $PV = nRT$

where $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

**Density of a gas**

Equation 10.3.9: $d = \frac{MP}{RT}$

## Conceptual Problems

1. For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?
2. What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?
3. Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

| Given | Solve for |
|---|---|
| $V_1$, $T_1$, $T_2$, $n_1$ | $n_2$ |
| $P_1$, $P_2$, $T_2$, $n_2$ | $n_1$ |
| $T_1$, $T_2$ | $V_2$ |
| $P_1$, $n_1$ | $P_2$ |

4. Given the following information and using the ideal gas law, what equation would you use to solve the problem?

| Given | Solve for |
|---|---|
| $P_1$, $P_2$, $T_1$ | $T_2$ |
| $V_1$, $n_1$, $n_2$ | $V_2$ |
| $T_1$, $T_2$, $V_1$, $V_2$, $n_2$ | $n_1$ |

5. Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?
6. Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.
    1. amount and volume
    2. pressure and amount
    3. temperature and volume
    4. temperature and amount
    5. pressure and temperature
7. Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

## Answer

1.
2.
3.
4.
5.
6. 1. $P/T$ = constant
    2. $V/T$ = constant (Charles' law)
    3. $P/n$ = constant
    4. $PV$ = constant (Boyle's law)
    5. $V/n$ = constant (Avogadro's law)
7.

## Numerical Problems

1. Calculate the number of moles in each sample at STP.
    1. 1580 mL of $NO_2$
    2. 847 $cm^3$ of HCl
    3. 4.792 L of $H_2$
    4. a 15.0 cm × 6.7 cm × 7.5 cm container of ethane
2. Calculate the number of moles in each sample at STP.
    1. 2200 $cm^3$ of $CO_2$
    2. 1200 $cm^3$ of $N_2$
    3. 3800 mL of $SO_2$
    4. 13.75 L of $NH_3$
3. Calculate the mass of each sample at STP.
    1. 36 mL of HI
    2. 550 L of $H_2S$
    3. 1380 $cm^3$ of $CH_4$
4. Calculate the mass of each sample at STP.
    1. 3.2 L of $N_2O$
    2. 65 $cm^3$ of $Cl_2$
    3. 3600 mL of HBr
5. Calculate the volume in liters of each sample at STP.

1. 1.68 g of Kr
2. 2.97 kg of propane ($C_3H_8$)
3. 0.643 mg of $(CH_3)_2O$

6. Calculate the volume in liters of each sample at STP.
   1. 3.2 g of Xe
   2. 465 mg of $CS_2$
   3. 5.34 kg of acetylene ($C_2H_2$)
7. Calculate the volume of each gas at STP.
   1. 1.7 L at 28°C and 96.4 kPa
   2. 38.0 mL at 17°C and 103.4 torr
   3. 650 mL at −15°C and 723 mmHg
8. Calculate the volume of each gas at STP.
   1. 2.30 L at 23°C and 740 mmHg
   2. 320 mL at 13°C and 97.2 kPa
   3. 100.5 mL at 35°C and 1.4 atm
9. One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?
10. An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

    $2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$

    At STP, what volume of $CO_2(g)$ is produced?
11. Calculate the density of ethylene ($C_2H_4$) under each set of conditions.
    1. 7.8 g at 0.89 atm and 26°C
    2. 6.3 mol at 102.6 kPa and 38°C
    3. 9.8 g at 3.1 atm and −45°C
12. Determine the density of $O_2$ under each set of conditions.
    1. 42 g at 1.1 atm and 25°C
    2. 0.87 mol at 820 mmHg and 45°C
    3. 16.7 g at 2.4 atm and 67°C
13. At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?
14. What volume must a balloon have to hold 6.20 kg of $H_2$ for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?
15. What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?
16. The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m$^3$, what is the average molecular mass of air?

## Answers

1. 1. $7.05 \times 10^{-2}$ mol
   2. $3.78 \times 10^{-2}$ mol
   3. 0.2138 mol
   4. $3.4 \times 10^{-2}$ mol

2.
3. 1. 0.21 g HI;
   2. 840 g $H_2S$;
   3. 0.988 g $CH_4$
4.
5. 1. 0.449 L Kr
   2. 1510 L $C_3H_8$
   3. $3.13 \times 10^{-4}$ L $(CH_3)_2O$
6.
7. 1. 1.5 L
   2. 4.87 mL
   3. 650 mL
8.
9. 281 mmHg
10.
11.
12. 1. 1.0 g/L
    2. 1.1 g/L
    3. 4.6 g/L
13.
14.
15.
16. 2174
17.

## Contributors

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# 10.4: The Combined Gas Law

**Learning Objectives**

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

We often encounter cases where two of the variables *P*, *V*, n and *T* are allowed to vary for a given sample of gas, and we are interested in the change in the value of the third under the new conditions. If we rearrange the ideal gas law so that *P*, *V*, and *T*, the quantities that change, are on one side and the constant terms (*R* and *n* for a given sample of gas) are on the other, we obtain

$$\frac{PV}{T} = nR = constant$$

Thus the quantity *PV*/n*T* is constant

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

In many of these problems one considers the changes in a sample of gas where the number of moles does not change. In such a case one can write the relationship as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

If two of the parameters specifying the thermodynamic state of the gas sample are held constant, one recovers simple proportional relationships among the other two which were experimentally observed centuries ago by

***Robert Boyle***

$V \propto \frac{1}{P}\,(at\ constant\ n,\ V)$

expresses the idea that at constant composition (e.g. the number of moles of gas) and temperature the product PV is a constant.

***Jacques Charles and Joseph-Louis Gay-Lussac***

$V \propto T\,(at\ constant\ n, P)$

expresses the idea that at constant composition (e.g. the number of moles of gas) and pressure the ratio V/T is a constant. Using Boyle's law this also can be written as P/T being constant

***Amedeo Avogadro***

$V \propto n\,(at\ constant\ T, P)$

In its original formulation, Avogadro's law stated that equal volumes of gas at constant temperature and pressure held the same number of molecules

Brief descriptions of these scientists work are found at the end of this section.

### Example 10.4.1

Charles originally observed the change of volume with temperature in balloon ascents and descents that he made. Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C. How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 5?

**Given:** temperature, pressure, amount, and volume in August; temperature in January

**Asked for:** volume in January

**Strategy:**

**A** Use the results from Example 5 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 86°F to 14°F. Begin by constructing a table showing the initial and final conditions.

**B** Rearrange the ideal gas law to isolate those quantities that differ between the initial and final states on one side of the equation, in this case *V* and *T*.

**C** Equate the ratios of those terms that change for the two sets of conditions. Making sure to use the appropriate units, insert the quantities and solve for the unknown parameter.

**Solution:**

**A** To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

| | August (initial) | January (final) |
|---|---|---|
| *T* | 30°C = 303 K | −10°C = 263 K |
| *P* | 0.980 atm | 0.980 atm |
| *n* | $1.23 \times 10^3$ mol $H_2$ | $1.23 \times 10^3$ mol $H_2$ |
| *V* | 31,150 L | ? |

Thus we are asked to calculate the effect of a change in temperature on the volume of a fixed amount of gas at constant pressure.

**B** Both $n$ and $P$ are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation 10.4.3 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

This is the relationship first noted by Charles.

**C** Solving the equation for $V_f$, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150 \text{ L} \times \frac{263 \text{ K}}{303 \text{ K}} = 2.70 \times 10^4 \text{ L}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume *must* be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

Exercise

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (*T* = −196°C). What is the final volume of the gas in the balloon?

**Answer:** 0.52 L

Example 8 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (*PV* = constant) and the relationship between volume and amount observed by Avogadro (*V*/*n* = constant). We will not do so for all cases, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 8 can be applied in *any* such case, as we demonstrate in Example 9 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

### Example 10.4.2

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 5 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

**Given:** initial volume, amount, temperature, and pressure; final temperature

**Asked for:** final pressure

**Strategy:**

Follow the strategy outlined in Example 8.

**Solution:**

Prepare a table to determine which parameters change and which are held constant:

| | Initial | Final |
|---|---|---|
| $V$ | 0.406 L | 0.406 L |
| $n$ | 0.025 mol | 0.025 mol |
| $T$ | 25°C = 298 K | 750°C = 1023 K |
| $P$ | 1.5 atm | ? |

Once again, two parameters are constant while one is varied, and we are asked to calculate the fourth. As before, we begin with the ideal gas law and rearrange it as necessary to get all the constant quantities on one side. In this case, because $V$ and $n$ are constant, we rearrange to obtain

$$P = \left(\frac{nR}{V}\right)(T) = constant \times T$$

Dividing both sides by $T$, we obtain an equation analogous to the one in Example 6, $P/T = nR/V$ = constant. Thus the ratio of $P$ to $T$ does not change if the amount and volume of a gas are held constant. We can thus write the relationship between any two sets of values of $P$ and $T$ for the same sample of gas at the same volume as

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

In this example, $P_i$ = 1.5 atm, $T_i$ = 298 K, and $T_f$ = 1023 K, and we are asked to find $P_f$. Solving for $P_f$ and substituting the appropriate values, we obtain

$$P_f = P_i \times \frac{T_f}{T_i} = 1.5 \text{ atm} \times \frac{1023 \text{ K}}{298 \text{ K}} = 5.1 \text{ atm}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Exercise

Suppose that a fire extinguisher, filled with $CO_2$ to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

**Answer:** 23.4 atm

### Example 10.4.3

We saw in Example 5 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained $1.23 \times 10^3$ mol of $H_2$ gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and −30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

**Given:** initial pressure, temperature, amount, and volume; final pressure and temperature

**Asked for:** final volume

**Strategy:**

Follow the strategy outlined in Example 6.

**Solution:**

Begin by setting up a table of the two sets of conditions:

| | Initial | Final |
|---|---|---|
| $P$ | 745 mmHg = 0.980 atm | 312 mmHg = 0.411 atm |
| $T$ | 30°C = 303 K | −30°C = 243 K |
| $n$ | $1.23 \times 10^3$ mol $H_2$ | $1.23 \times 10^3$ mol $H_2$ |
| $V$ | 31,150 L | ? |

Thus all the quantities except $V_2$ are known. Solving Equation 10.4.3 for $V_2$ and substituting the appropriate values give

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} = 3.115 \times 10^4 \text{ L} \times \frac{0.980 \cancel{\text{ atm}}}{0.411 \cancel{\text{ atm}}}\frac{243 \cancel{\text{ K}}}{303 \cancel{\text{ K}}} = 5.96 \times 10^4 \text{ L}$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both $T$ and $1/P$, the variable that changes the most will have the greatest effect on $V$. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for $V$ and then substituting the relevant parameters for an altitude of 23,000 ft:

$$V = \frac{nRT}{P} = \frac{\left(1.23 \times 10^3 \cancel{\text{ mol}}\right)\left[0.082057 \left(L \cdot \cancel{\text{atm}}\right) / \left(\cancel{\text{K}} \cdot \cancel{\text{mol}}\right)\right]\left(243 \cancel{\text{ K}}\right)}{0.411 \cancel{\text{ atm}}} = 5.97 \times 10^4 L$$

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

Exercise

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

**Answer:** $4.07 \times 10^3$

## The Relationship between Pressure and Volume

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

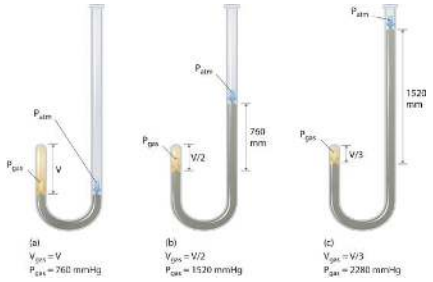
## Robert Boyle (1627–1691)

Boyle, the youngest (and 14th!) child of the Earl of Cork, was an important early figure in chemistry whose views were often at odds with accepted wisdom. Boyle's studies of gases are reported to have utilized a very tall J-tube that he set up in the entryway of his house, which was several stories tall. He is known for the gas law that bears his name and for his book, *The Sceptical Chymist*, which was published in 1661 and influenced chemists for many years after his death. In addition, one of Boyle's early essays on morals is said to have inspired Jonathan Swift to write *Gulliver's Travels*.

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 10.4.1. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure *plus* the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 10.4.2 ). A simple plot of *V* versus *P* gives a curve called a *hyperbola* and reveals an *inverse* relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

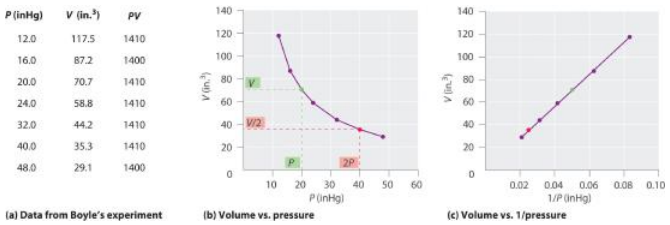
(\ PV = constant \tag{10.4.7} \)

**Figure 10.4.1 Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume**




*(a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is V/2. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to V/3.*

**Figure10.4.2 Plots of Boyle's Data**



| P (inHg) | V (in.$^3$) | PV |
|---|---|---|
| 12.0 | 117.5 | 1410 |
| 16.0 | 87.2 | 1400 |
| 20.0 | 70.7 | 1410 |
| 24.0 | 58.8 | 1410 |
| 32.0 | 44.2 | 1410 |
| 40.0 | 35.3 | 1410 |
| 48.0 | 29.1 | 1400 |



*(a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.$^3$ rather than cm$^3$) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P.*

Dividing both sides by *P* gives an equation illustrating the inverse relationship between *P* and *V*:

$$V = \frac{constant}{P} = constant\left(\frac{1}{P}\right) \; or \; V \propto \frac{1}{P}$$

where the ∝ symbol is read “is proportional to.” A plot of $V$ versus $1/P$ is thus a straight line whose slope is equal to the constant in Equation 10.4.7. Dividing both sides of Equation 10.4.7 by $V$ instead of $P$ gives a similar relationship between $P$ and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle’s lawA law that states that at constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure., after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.*

## The Relationship between Temperature and Volume

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles’s initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of $V$ versus $T$ was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to −273.15°C (Figure 9.3.1 ) or absolute zero. A sample of a real gas cannot *really* have a volume of zero because any sample of matter must have *some* volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. However, the ideal gas model does allow for reaching absolute zero, but the second law of thermodynamics, which will be discussed in Unit 7, makes this impossible.

### Jacques Alexandre César Charles (1746–1823) and Joseph-Louis Gay-Lussac (1778–1850)

In 1783, Charles filled a balloon (“aerostatic globe”) with hydrogen (generated by the reaction of iron with more than 200 kg of acid over several days) and flew successfully for almost an hour. When the balloon descended in a nearby village, however, the terrified townspeople destroyed it. In 1804, Gay-Lussac managed to ascend to 23,000 ft (more than 7000 m) to collect samples of the atmosphere to analyze its composition as a function of altitude. In the process, he had trouble breathing and nearly froze to death, but he set an altitude record that endured for decades. (To put Gay-Lussac’s achievement in perspective, recall that modern jetliners cruise at only 35,000 ft!)

We can state Charles’s and Gay-Lussac’s findings in simple terms: *At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in Kelvin).* This relationship is often referred to as Charles’s law

Charles’s law is valid for virtually all gases at temperatures well above their boiling points. *Note that the temperature must be expressed in kelvins,* not *in degrees Celsius.*

## The Relationship between Amount and Volume

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac’s work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles. (This is the historic “Avogadro’s hypothesis” introduced in Section 1.3.) A logical corollary, sometimes called Avogadro’s lawA law that states that at constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample., describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = (constant)\,(n) \; or \; V \propto n \; (at \; constant \; T \; and \; P)$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

## Summary

Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at −273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

## Key Takeaway

- The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas.

## Conceptual Problems

1. Sketch a graph of the volume of a gas versus the pressure on the gas. What would the graph of $V$ versus $P$ look like if volume was directly proportional to pressure?
2. What properties of a gas are described by Boyle's law, Charles's law, and Avogadro's law? In each law, what quantities are held constant? Why does the constant in Boyle's law depend on the amount of gas used and the temperature at which the experiments are carried out?
3. Use Charles's law to explain why cooler air sinks.
4. Use Boyle's law to explain why it is dangerous to heat even a small quantity of water in a sealed container.

For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?

For a given amount of a gas, the volume, temperature, and pressure under any one set of conditions are related to the volume, the temperature, and the pressure under any other set of conditions by the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Derive this equation from the ideal gas law. At constant temperature, this equation reduces to one of the laws discussed in Section 10.3; which one? At constant pressure, this equation reduces to one of the laws discussed in this section; which one?

Predict the effect of each change on one variable if the other variables are held constant.

1. If the number of moles of gas increases, what is the effect on the temperature of the gas?
2. If the temperature of a gas decreases, what is the effect on the pressure of the gas?
3. If the volume of a gas increases, what is the effect on the temperature of the gas?
4. If the pressure of a gas increases, what is the effect on the number of moles of the gas?

What would the ideal gas law be if the following were true?

1. volume were proportional to pressure
2. temperature were proportional to amount
3. pressure were inversely proportional to temperature
4. volume were inversely proportional to temperature
5. both pressure and volume were inversely proportional to temperature

Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

| Given | Solve for |
|---|---|
| $V_1$, $T_1$, $T_2$, $n_1$ | $n_2$ |
| $P_1$, $P_2$, $T_2$, $n_2$ | $n_1$ |
| $T_1$, $T_2$ | $V_2$ |
| $P_1$, $n_1$ | $P_2$ |

Given the following information and using the ideal gas law, what equation would you use to solve the problem?

| Given | Solve for |
|---|---|
| $P_1$, $P_2$, $T_1$ | $T_2$ |
| $V_1$, $n_1$, $n_2$ | $V_2$ |
| $T_1$, $T_2$, $V_1$, $V_2$, $n_2$ | $n_1$ |

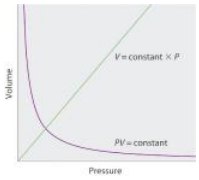
Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?

Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.

1. amount and volume
2. pressure and amount
3. temperature and volume
4. temperature and amount
5. pressure and temperature

Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

## Answer

1. 

2.
3.

## Numerical Problems

1. A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.
    1. The pressure is changed to 85.7 mmHg. How many milliliters does the gas occupy?
    2. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
    3. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
    4. The sample is heated to 30°C. What is the volume in liters?
    5. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?
2. A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?
    1. m

    A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.

    At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?

One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is AlCl3. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?

An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

$2\ C2H2(g) + 5\ O2(g) \rightarrow 4\ CO2(g) + 2\ H2O(l)$

At STP, what volume of CO2(g) is produced?

Calculate the density of ethylene (C2H4) under each set of conditions.

1. 7.8 g at 0.89 atm and 26°C
2. 6.3 mol at 102.6 kPa and 38°C
3. 9.8 g at 3.1 atm and −45°C

Determine the density of O2 under each set of conditions.

1. 42 g at 1.1 atm and 25°C
2. 0.87 mol at 820 mmHg and 45°C
3. 16.7 g at 2.4 atm and 67°C

At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?

What volume must a balloon have to hold 6.20 kg of H2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?

What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?

A typical automobile tire is inflated to a pressure of 28.0 lb/in.$^2$ Assume that the tire is inflated when the air temperature is 20°C; the car is then driven at high speeds, which increases the temperature of the tire to 43°C. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?

The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m$^3$, what is the average molecular mass of air?

Kerosene has a self-ignition temperature of 255°C. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of 23°C is pressurized, at what pressure would the kerosene vapor ignite?

## Answer

1. 1. $1.99 \times 10^5$ mL
   2. $6.19 \times 10^4$ mmHg
   3. 7270°C
   4. 22.8 L
   5. 51.4 K
2.

## Contributors

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# 10.5: Gas Mixtures

**Learning Objectives**

- To determine the contribution of each component gas to the total pressure of a mixture of gases.

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

## Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{10.5.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

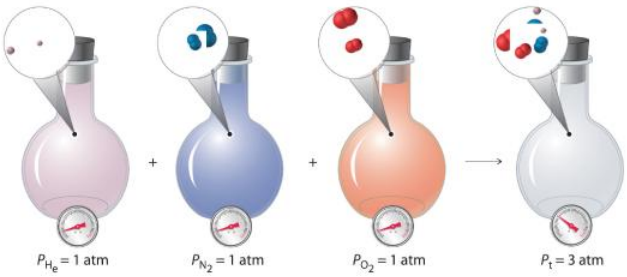
With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressureThe pressure a gas in a mixture would exert if it were the only one present (at the same temperature and volume)., the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, *the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases*. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as Dalton's law of partial pressuresA law that states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases.. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{10.5.2}$$

where $P_t$ is the total pressure and the other terms are the partial pressures of the individual gases (Figure 10.5.1).

**Figure 10.5.1 Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.**




For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{10.5.3}$$

More generally, for a mixture of *i* components, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{10.5.4a}$$

$$P_{tot} = \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{10.5.4b}$$

Equation 10.5.4. restates Equation 10.5.3 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on *only* the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 10.27 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 11.

### Example 10.5.1

For reasons that we will examine in Chapter 15, deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called “the bends.” At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of $O_2$ and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

**Given:** masses of components, total volume, and temperature

**Asked for:** partial pressures and total pressure

**Strategy:**

**A** Calculate the number of moles of He and $O_2$ present.

**B** Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

**Solution:**

**A** The number of moles of He is

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol}$$

The number of moles of $O_2$ is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol}$$

**B** We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm}$$

Exercise

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

**Answer:** $P(CH_4)$ = 137 atm; $P(C_2H_6)$ = 13.4 atm; $P_t$ = 151 atm.

## Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction ($X$)The ratio of the number of moles of any component of a mixture to the total number of moles of all species present in the mixture. of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture ($n_t$):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{10.5.6}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $X_A$ = 1.0, then the sample is pure A, not a mixture. If $X_A$ = 0, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_t = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{10.5.7}$$

Rearranging this equation gives

$$P_A = x_A P_{tot} \tag{10.5.8}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. Recall from Chapter 7 (Table 7.6.1) that by volume, Earth's atmosphere is about 78% $N_2$, 21% $O_2$, and 0.9% Ar, with trace amounts of gases such as $CO_2$, $H_2O$, and others. This means that 78% of the particles present in the atmosphere are $N_2$; hence the mole fraction of $N_2$ is 78%/100% = 0.78. Similarly, the mole fractions of $O_2$ and Ar are 0.21 and 0.009, respectively. Using Equation 10.5.4, we therefore know that the partial pressure of $N_2$ is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of $O_2$ and Ar are 0.21 and 0.009 atm, respectively.

### Example 10.5.2

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

| | Inhaled Air (mmHg) | Exhaled Air (mmHg) |
|---|---|---|
| $P_{N_2}$ | 597 | 568 |
| $P_{O_2}$ | 158 | 116 |
| $P_{H_2O}$ | 0.3 | 28 |
| $P_{CO_2}$ | 5 | 48 |
| $P_{Ar}$ | 8 | 8 |
| $P_t$ | 767 | 767 |

**Given:** pressures of gases in inhaled and exhaled air

**Asked for:** mole fractions of gases in exhaled air

**Strategy:**

Calculate the mole fraction of each gas using Equation 10.5.8.

**Solution:**

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}}$$

where $P_A$ is the partial pressure of A and $P_t$ is the total pressure. In this case,

$$x_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of $P_A$ and $X_A$ for exhaled air.

| $P_A$ | | $X_A$ |
|---|---|---|
| $N_2$ | $\left(568 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.747 \ atm$ | $\frac{0.747 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.740$ |
| $O_2$ | $\left(116 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.153 \ atm$ | $\frac{0.153 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.151$ |
| $H_2O$ | $\left(28 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.037 \ atm$ | $\frac{0.031 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.031$ |
| $CO_2$ | $\left(48 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.063 \ atm$ | $\frac{0.063 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.061$ |
| Ar | $\left(8 \ \cancel{mmHg}\right) \frac{1 \ atm}{760 \ \cancel{mmHg}} = 0.011 \ atm$ | $\frac{0.011 \ \cancel{atm}}{1.01 \ \cancel{atm}} = 0.011$ |

Exercise

We saw in Example 10 that Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% $CO_2$ and 3% $N_2$, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of $CO_2$ and $N_2$.

**Answer:** $P_{CO_2} = 86$ atm, $P_{N_2} = 2.7$ atm

## Summary

The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

## Key Takeaway

- The partial pressure of each gas in a mixture is proportional to its mole fraction.

## Key Equations

**Mole fraction**

Equation 10.5.7: $X_A = \frac{molesA}{totalmoles} = \frac{n_A}{n_t}$

**Relationship between partial pressure and mole fraction**

Equation 10.5.8: $P_A = X_A P_t$

## Conceptual Problems

1. Dalton's law of partial pressures makes one key assumption about the nature of the intermolecular interactions in a mixture of gases. What is it?

2. What is the relationship between the partial pressure of a gas and its mole fraction in a mixture?

## Numerical Problems

1. What is the partial pressure of each gas if the following amounts of substances are placed in a 25.0 L container at 25°C? What is the total pressure of each mixture?
    1. 1.570 mol of $CH_4$ and 0.870 mol of $CO_2$
    2. 2.63 g of CO and 1.24 g of $NO_2$
    3. 1.78 kg of $CH_3Cl$ and 0.92 kg of $SO_2$
2. What is the partial pressure of each gas in the following 3.0 L mixtures at 37°C as well as the total pressure?
    1. 0.128 mol of $SO_2$ and 0.098 mol of methane ($CH_4$)
    2. 3.40 g of acetylene ($C_2H_2$) and 1.54 g of He
    3. 0.267 g of NO, 4.3 g of Ar, and 0.872 g of $SO_2$
3. In a mixture of helium, oxygen, and methane in a 2.00 L container, the partial pressures of He and $O_2$ are 13.6 kPa and 29.2 kPa, respectively, and the total pressure inside the container is 95.4 kPa. What is the partial pressure of methane? If the methane is ignited to initiate its combustion with oxygen and the system is then cooled to the original temperature of 30°C, what is the final pressure inside the container (in kilopascals)?
4. A 2.00 L flask originally contains 1.00 g of ethane ($C_2H_6$) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce $CO_2$ and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure and the partial pressure of each gas before and after the reaction.
5. If a 20.0 L cylinder at 19°C is charged with 5.0 g each of sulfur dioxide and oxygen, what is the partial pressure of each gas? The sulfur dioxide is ignited in the oxygen to produce sulfur trioxide gas, and the mixture is allowed to cool to 19°C at constant pressure. What is the final volume of the cylinder? What is the partial pressure of each gas in the piston?
6. The highest point on the continent of Europe is Mt. Elbrus in Russia, with an elevation of 18,476 ft. The highest point on the continent of South America is Mt. Aconcagua in Argentina, with an elevation of 22,841 ft.
    1. The following table shows the variation of atmospheric pressure with elevation. Use the data in the table to construct a plot of pressure versus elevation.

| Elevation (km) | Pressure in Summer (mmHg) | Pressure in Winter (mmHg) |
|---|---|---|
| 0.0 | 760.0 | 760.0 |
| 1.0 | 674.8 | 670.6 |
| 1.5 | 635.4 | 629.6 |
| 2.0 | 598.0 | 590.8 |
| 3.0 | 528.9 | 519.7 |
| 5.0 | 410.6 | 398.7 |
| 7.0 | 314.9 | 301.6 |
| 9.0 | 237.8 | 224.1 |

    2. Use your graph to estimate the pressures in millimeters of mercury during the summer and the winter at the top of both mountains in both atmospheres and kilopascals.
    3. Given that air is 20.95% $O_2$ by volume, what is the partial pressure of oxygen in atmospheres during the summer at each location?

## Answers

1. 1. P($CH_4$) = 1.54 atm, P($CO_2$) = 0.851 atm, $P_T$ = 2.39 atm
   2. *P(CO)* = 0.0918 atm, P($NO_2$) = 0.0264 atm, $P_T$ = 0.1182 atm
   3. P( CH3Cl) = 34.5 atm, P($SO_2$) = 14 atm, $P_T$ = 49 atm
2. 
3. 52.6 kPa, 66.2 kPa
4. 
5. 
6. 

## Contributors

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# 10.6: Stoichiometry Involving Gases

**Learning Objectives**

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing. As a chemical engineer said to one of the authors, “Gases always go where you want them to, liquids sometimes do, but solids almost never do.”

## Example 10.6.1

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give $SO_2$, followed by the reaction of $SO_2$ with $O_2$ in the presence of a catalyst to give $SO_3$, which reacts with water to give $H_2SO_4$. The overall chemical equation is as follows:

$$2S(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$$

What volume of $O_2$ (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton of $H_2SO_4$?

**Given:** reaction, temperature, pressure, and mass of one product

**Asked for:** volume of gaseous reactant

**Strategy:**

**A** Calculate the number of moles of $H_2SO_4$ in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of $O_2$ required.

**B** Use the ideal gas law to determine the volume of $O_2$ required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

**Solution:**

We can see from the stoichiometry of the reaction that 3/2 mol of $O_2$ is required to produce 1 mol of $H_2SO_4$. This is a standard stoichiometry problem of the type presented in Chapter 7, except this problem asks for the volume of one of the reactants ($O_2$) rather than its mass. We proceed exactly as in Chapter 7, using the strategy

mass of $H_2SO_4$ → moles $H_2SO_4$ → moles $O_2$ → liters $O_2$

**A** We begin by calculating the number of moles of $H_2SO_4$ in 1.00 tn:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4$$

We next calculate the number of moles of $O_2$ required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3\text{mol } O_2}{2\text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2$$

**B** After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of $O_2$:

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 tn of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Exercise

In Example 5, we saw that Charles used a balloon containing approximately 31,150 L of $H_2$ for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

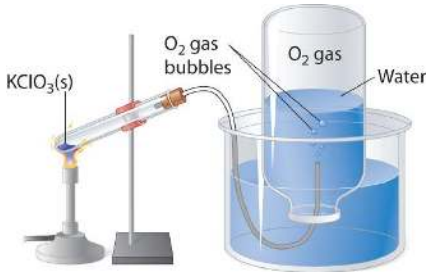
$Fe(s) + 2\ HCl(aq) \rightarrow H_2(g) + FeCl_2(aq)$

How much iron (in kilograms) was needed to produce this volume of $H_2$ if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

**Answer:** 68.6 kg of Fe (approximately 150 lb)

Many of the advances made in chemistry during the 18th and 19th centuries were the result of careful experiments done to determine the identity and quantity of gases produced in chemical reactions. For example, in 1774, Joseph Priestley was able to isolate oxygen gas by the thermal decomposition of mercuric oxide (HgO). In the 1780s, Antoine Lavoisier conducted experiments that showed that combustion reactions, which require oxygen, produce what we now know to be carbon dioxide. Both sets of experiments required the scientists to collect and manipulate gases produced in chemical reactions, and both used a simple technique that is still used in chemical laboratories today: collecting a gas by the displacement of water. As shown in Figure 10.6.1 , the gas produced in a reaction can be channeled through a tube into inverted bottles filled with water. Because the gas is less dense than liquid water, it bubbles to the top of the bottle, displacing the water. Eventually, all the water is forced out and the bottle contains only gas. If a calibrated bottle is used (i.e., one with markings to indicate the volume of the gas) and the bottle is raised or lowered until the level of the water is the same both inside and outside, then the pressure within the bottle will exactly equal the atmospheric pressure measured separately with a barometer.

**Figure 10.6.1 An Apparatus for Collecting Gases by the Displacement of Water**




*When $KClO_3(s)$ is heated, $O_2$ is produced according to the equation $[ KClO_{3}\left ( s \right ) \rightarrow KCl\left ( s \right )+\dfrac{3}{2} O_{2}\left ( g \right )$ \notag $]$. The oxygen gas travels through the tube, bubbles up through the water, and is collected in a bottle as shown.*

The only gases that cannot be collected using this technique are those that readily dissolve in water (e.g., $NH_3$, $H_2S$, and $CO_2$) and those that react rapidly with water (such as $F_2$ and $NO_2$). Remember, however, when calculating the amount of gas formed in the reaction, the gas collected inside the bottle is *not* pure. Instead, it is a mixture of the product gas and water vapor. As we will discuss in Chapter 11 , all liquids (including water) have a measurable amount of vapor in equilibrium with the liquid because molecules of the liquid are continuously escaping from the liquid's surface, while other molecules from the vapor phase collide with the surface and return to the liquid. The vapor thus exerts a pressure above the liquid, which is called the liquid's *vapor pressure*. In the case shown in Figure 10.6.1 the bottle is therefore actually filled with a mixture of $O_2$ and water vapor, and the total pressure is, by Dalton's law of partial pressures, the sum of the pressures of the two components:

$$P_{\text{tot}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} = P_{\text{bar.}} \tag{10.6.1}$$

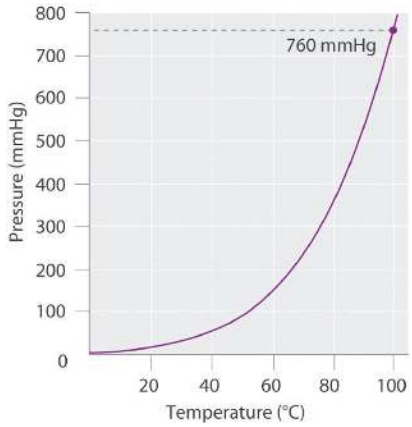
If we want to know the pressure of the gas generated in the reaction to calculate the amount of gas formed, we must first subtract the pressure due to water vapor from the total pressure. This is done by referring to tabulated values of the vapor pressure of water as a function of temperature (Table 10.6.1 ). As shown in Figure 10.6.2, the vapor pressure of water increases rapidly with

increasing temperature, and at the normal boiling point (100°C), the vapor pressure is exactly 1 atm. The methodology is illustrated in Example 14.

**Table 10.6.1 Vapor Pressure of Water at Various Temperatures**

| *T* (°C) | *P* (in mmHg) | *T* | *P* | *T* | *P* | *T* | *P* |
|---|---|---|---|---|---|---|---|
| 0 | 4.58 | 21 | 18.66 | 35 | 42.2 | 92 | 567.2 |
| 5 | 6.54 | 22 | 19.84 | 40 | 55.4 | 94 | 611.0 |
| 10 | 9.21 | 23 | 21.08 | 45 | 71.9 | 96 | 657.7 |
| 12 | 10.52 | 24 | 22.39 | 50 | 92.6 | 98 | 707.3 |
| 14 | 11.99 | 25 | 23.77 | 55 | 118.1 | 100 | 760.0 |
| 16 | 13.64 | 26 | 25.22 | 60 | 149.5 | 102 | 815.8 |
| 17 | 14.54 | 27 | 26.75 | 65 | 187.7 | 104 | 875.1 |
| 18 | 15.48 | 28 | 28.37 | 70 | 233.8 | 106 | 937.8 |
| 19 | 16.48 | 29 | 30.06 | 80 | 355.3 | 108 | 1004.2 |
| 20 | 17.54 | 30 | 31.84 | 90 | 525.9 | 110 | 1074.4 |

**Figure 10.6.2 A Plot of the Vapor Pressure of Water versus Temperature.**




*The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.*

## Example 10.6.2

Sodium azide ($NaN_3$) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na_{(s)} + 3N_{2\ (g)}$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the $N_2$ gas that results from the decomposition of a 5.00 g sample of $NaN_3$ could be collected by displacing water from an inverted flask, as in Figure 10.6.1, what volume of gas would be produced at 22°C and 762 mmHg?

**Given:** reaction, mass of compound, temperature, and pressure

**Asked for:** volume of nitrogen gas produced

**Strategy:**

**A** Calculate the number of moles of $N_2$ gas produced. From the data in Table 10.6.1, determine the partial pressure of $N_2$ gas in the flask.

**B** Use the ideal gas law to find the volume of $N_2$ gas produced.

**Solution:**

**A** Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of $N_2$ gas produced:

[\rm\dfrac{5.00\;g\;NaN_3}{(22.99+3\times14.01)\;g/mol}\times\dfrac{3mol\;N_2}{2mol\;NaN_3}=0.115\;mol\; N_2 \notag \]

The pressure given (762 mmHg) is the *total* pressure in the flask, which is the sum of the pressures due to the $N_2$ gas and the water vapor present. Table 10.6.1 tells us that the vapor pressure of water is 19.84 mmHg at 22°C (295 K), so the partial pressure of the $N_2$ gas in the flask is only 762 − 19.84 = 742 mmHg = 0.976 atm.

**B** Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\text{ mol} \times 0.08206\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 294\text{ K}}{0.978\text{ atm}} = 2.84\text{ L}$$

Exercise

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce $H_2$ gas according to the equation Zn(s) + 2 HCl(aq) → $H_2$(g) + $ZnCl_2$(aq). The resulting $H_2$ gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

**Answer:** 0.397 L

## Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

## Key Takeaway

- The ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

## Conceptual Problems

1. Why are so many industrially important reactions carried out in the gas phase?
2. The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?
3. Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

## Numerical Problems

1. Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?

1. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of $O_2$
2. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of $H_2$
3. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of $O_2$

2. During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of $CO_2$ at STP is produced,
    1. what mass of CO is consumed?
    2. what volume of CO at STP is consumed?
    3. how much $O_2$ (in liters) at STP is used?
    4. what mass of carbon is consumed?
    5. how much iron metal (in grams) is produced?
3. Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.
    1. What is the mass of $KClO_3$ in the original sample?
    2. What mass of oxygen is produced?
    3. What is the volume of oxygen produced at STP?
4. The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of $CO_2$ and 72.9 mL of $H_2O$ vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.
5. The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of $CO_2$ and 164 mL of $H_2O$ vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

## Answers

1. 
2. 
3. 
    1. 2.20 g $KClO_3$
    2. 0.863 g $O_2$
    3. 604 mL $O_2$
4. 
5. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

## Contributors

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# 10.7: The Kinetic Theory of Gases

**Learning Objectives**

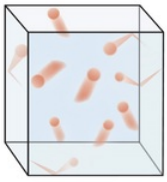
- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

## A Molecular Description

The kinetic molecular theory of gasesA theory that describes, on the molecular level, why ideal gases behave the way they do. explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

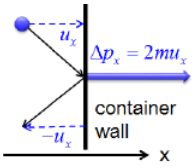
1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.



Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of ideal gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 10.7.1).

**Figure 10.7.1 Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall.**




*$u_x$ and $\Delta p_x$ are the $x$ component of the molecular velocity and the momentum transfered to the wall, respectively. The wall is perpendicular to $x$ axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.*

The **momentum transfer** to the wall perpendicular to $x$ axis as a molecule with an initial velocity $u_x$ in $x$ direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{10.7.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{10.7.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{10.7.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace $u_x^2$ in the expression above with the average value of $u_x^2$, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{10.7.4}$$

Finally, we must consider that there is nothing special about $x$ direction. We should expect that $\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}$. Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed ($u^2$) over all molecules. Since $u^2 = u_x^2 + u_y^2 + u_z^2$ for each molecule, $\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$. By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{10.7.5}$$

Anything that increases the frequency with which the molecules strike the walls or increases the momentum of the gas molecules (i.e., how hard they hit the walls) increases the pressure; anything that decreases that frequency or the momentum of the molecules decreases the pressure.

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. It refers to the *average translational* kinetic energy of the molecules of a gas which can be represented as $(\overline{e_K})$, *and states that at a given Kelvin temperature* $(T)$, *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{10.7.6}$$

where $N_A$ is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by $N_A$:

$$N_A\overline{e_K} = \frac{1}{2} M\overline{u^2} = \frac{3}{2}RT \tag{10.7.7}$$

where $M$ is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$.

By rearranging the equation, we can get the relationship between the root-mean square speed ($u_{\text{rms}}$) and the temperature.

The rms speed ($u_{\text{rms}}$) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{10.7.8}$$

where $N$ is the number of particles and $u_i$ is the speed of particle $i$.

The relationship between $u_{\text{rms}}$ and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{10.7.9}$$

In this equation, $u_{\text{rms}}$ has units of meters per second; consequently, the units of molar mass $M$ are kilograms per mole, temperature $T$ is expressed in kelvins, and the ideal gas constant $R$ has the value 8.3145 J/(K·mol).

The equation shows that $u_{\text{rms}}$ of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

*The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed ($v_p$) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 6.33 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and $v_p$ increases.*

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, *not* the same average speed. In contrast, the most probable speed ($v_p$) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 10.33 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and $v_p$ increases.

### Note the Pattern

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

### Example 10.7.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed ($v_{\text{av}}$) root mean square speed ($v_{\text{rms}}$), and most probable speed ($v_p$).

**Given:** particle speeds

**Asked for:** average speed ($v_{\text{av}}$) root mean square speed ($v_{\text{rms}}$), and most probable speed ($v_p$)

**Strategy:**

Use Equation 10.7.9 to calculate the average speed and Equation 10.7.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

**Solution:**

The average speed is the sum of the speeds divided by the number of particles:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_p$ = 6.0 m/s. The $v_{\text{rms}}$ of the

particles, which is related to the average kinetic energy, is greater than their average speed.

Exercise

Ten particles were found to have speeds of 0.1, 1.0, 2.0, 3.0, 3.0, 3.0, 4.0, 4.0, 5.0, and 6.0 m/s. Calculate their average speed ($v_{av}$) root mean square speed ($v_{rms}$), and most probable speed ($v_p$).

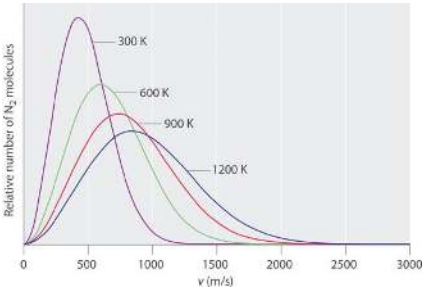
**Answer:**

$$\bar{v} = 3.1\ m/s;\ v_{rms} = 3.5\ m/s; v_p = 3.0 m/s$$

## Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction, as you will learn in Chapter 14. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 10.7.2 . Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure 10.7.2 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributionsA curve that shows the distribution of molecular speeds at a given temperature., after one of the other major figures responsible for the kinetic molecular theory of gases.

**Figure 10.7.2 The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperature.**




*Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.*

## The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

## Pressure versus Volume

At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.

## Volume versus Temperature

Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase

in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.

## Pressure of Gas Mixtures

Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

### Example 10.7.2

The temperature of a 4.75 L container of $N_2$ gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

1. average kinetic energy of the $N_2$ molecules?
2. rms speed of the $N_2$ molecules?
3. average speed of the $N_2$ molecules?
4. impact of each $N_2$ molecule on the wall of the container during a collision with the wall?
5. total number of collisions per second of $N_2$ molecules with the walls of the entire container?
6. number of collisions per second of $N_2$ molecules with each square centimeter of the container wall?
7. pressure of the $N_2$ gas?

**Given:** temperatures and volume

**Asked for:** effect of increase in temperature

**Strategy:**

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

**Solution:**

1. Increasing the temperature increases the average kinetic energy of the $N_2$ molecules.
2. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
3. If the rms speed of the $N_2$ molecules increases, the average speed also increases.
4. If, on average, the particles are moving faster, then they strike the container walls with more energy.
5. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
6. The number of collisions per second of $N_2$ molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
7. The pressure exerted by the $N_2$ gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

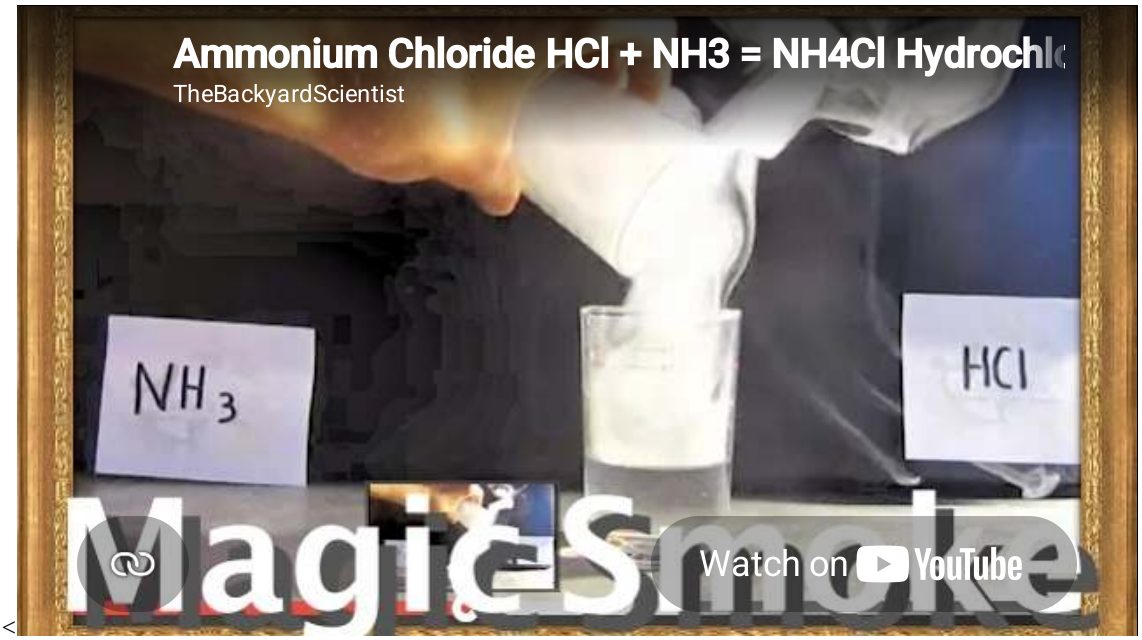
1. average kinetic energy of the He atoms?
2. rms speed of the He atoms?
3. average speed of the He atoms?
4. impact of each He atom on the wall of the container during a collision with the wall?
5. total number of collisions per second of He atoms with the walls of the entire container?
6. number of collisions per second of He atoms with each square centimeter of the container wall?
7. pressure of the He gas?

**Answer:** a. no change; b. no change; c. no change; d. no change; e. decreases; f. decreases; g. decreases

## Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment. Figure 10.7.3 shows white fumes of solid ammonium chloride ($NH_4Cl$) forming when containers of aqueous ammonia and HCl are placed near each other, even with no draft to stir the air. This phenomenon suggests that $NH_3$ and HCl molecules (as well as the more complex organic molecules responsible for the aromas of pizza and perfumes) move without assistance.

**Figure 10.7.3 The Diffusion of Gaseous Molecules.**







*When open containers of aqueous $NH_3$ and HCl are placed near each other in a draft-free environment, molecules of the two substances diffuse, collide, and react to produce white fumes of solid ammonium chloride ($NH_4Cl$). (From the Backyard Scientist)*

DiffusionThe gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with a uniform composition. is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. As we shall see in Chapter 11 , Chapter 12 , and Chapter 13 , diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. We can describe the phenomenon shown in Figure 10.7.3 by saying that the molecules of HCl and $NH_3$ are able to diffuse away from their containers, and that $NH_4Cl$ is formed where the two

gases come into contact. Similarly, we say that a perfume or an aroma diffuses throughout a room or a house. The related process, effusionThe escape of a gas through a small (usually microscopic) opening into an evacuated space., is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship,

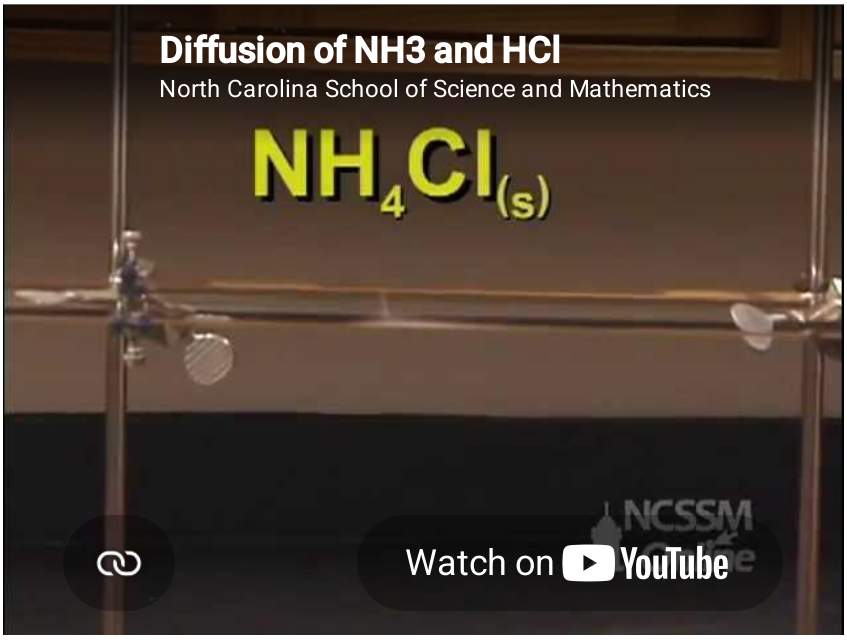
$$rate \propto \frac{1}{\sqrt{M}}$$

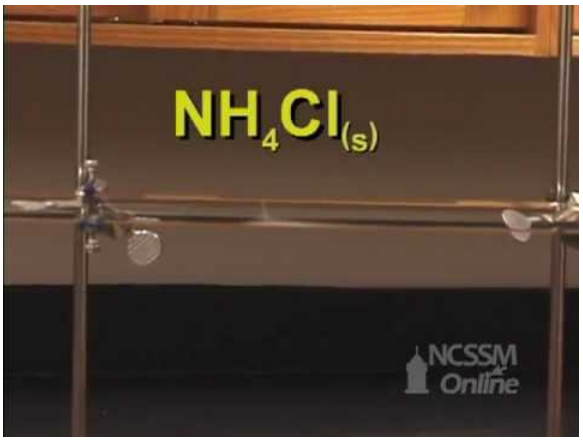
is referred to as Graham's lawA law that states that the rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass., after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses. If *r* is the effusion rate and *M* is the molar mass, then

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{10.7.10}$$

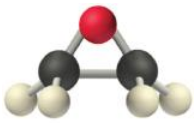
Although diffusion and effusion are different phenomena, the rate of diffusion is closely approximated using Equation 10.7.10 that is, if $M_1 < M_2$, then gas #1 will diffuse more rapidly than gas #2. This point is illustrated by the experiment shown in Figure 10.7.4 , which is a more quantitative version of the case shown in Figure 10.7.3 . The reaction is the same [$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(g)$], but in this experiment, two cotton balls containing aqueous ammonia and HCl are placed along a meter stick in a draft-free environment, and the position at which the initial $NH_4Cl$ fumes appear is noted. The white cloud forms much nearer the HCl-containing ball than the $NH_3$-containing ball. Because ammonia ($M$ = 17.0 g/mol) diffuses much faster than HCl ($M$ = 36.5 g/mol), the $NH_4Cl$ fumes form closer to HCl because the HCl molecules travel a shorter distance. The ratio of the distances traveled by $NH_3$ and HCl in is about 1.7, in reasonable agreement with the ratio of 1.47 predicted by their molar masses [$(36.5/17.0)^{1/2} = 1.47$].

**Figure 10.7.4 A Simple Experiment to Measure the Relative Rates of the Diffusion of Two Gases**




*Cotton balls containing aqueous $NH_3$ (left) and HCl (right) are placed a measured distance apart in a draft-free environment, and the position at which white fumes of $NH_4Cl$ first appear is noted. The puff of white $NH_4Cl$ forms much closer to the HCl-containing ball than to the $NH_3$-containing ball. The left edge of the white puff marks where the reaction was first observed. The position of the white puff (18.8 − 3.3 = 15.5 cm from the $NH_3$, 28.0 − 18.8 = 9.2 cm from the HCl, giving a ratio of distances of 15.5/9.2 = 1.7) is approximately the location predicted by Graham's law based on the square root of the inverse ratio of the molar masses of the reactants (1.47).*

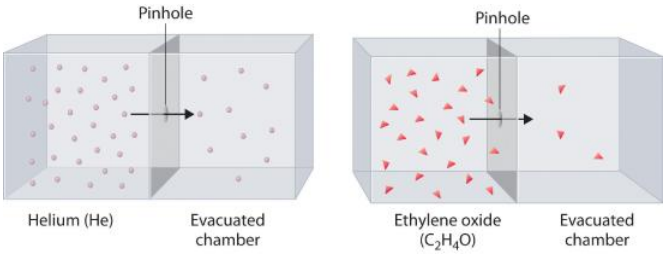

Ethylene oxide

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure 10.7.5for ethylene oxide and helium. Helium ($M$ = 4.00 g/mol) effuses much more rapidly than ethylene oxide ($M$ = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon

$$\sqrt{\frac{29}{4.00}} = 2.7$$

times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Mylar balloons can retain their helium for days.

**Figure 10.7.5 The Relative Rates of Effusion of Two Gases with Different Masses**




*The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide ($C_2H_4O$) molecules (M = 44.0 g/mol), as predicted by Graham's law.*

### Note the Pattern

At a given temperature, heavier molecules move more slowly than lighter molecules.

### Example 10.7.3

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of $^{235}U$. Naturally occurring uranium is only 0.720% $^{235}U$, whereas most of the rest (99.275%) is $^{238}U$, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound $UF_6$ (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which $UF_6$ is allowed to pass through a porous barrier. (The atomic mass of $^{235}U$ is 235.04, and the atomic mass of $^{238}U$ is 238.05.)
2. If *n* identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the *n*th power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

**Given:** isotopic content of naturally occurring uranium and atomic masses of $^{235}U$ and $^{238}U$

**Asked for:** ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

**Strategy:**

**A** Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.

**B** Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

**Solution:**

1. **A** The first step is to calculate the molar mass of $UF_6$ containing $^{235}U$ and $^{238}U$. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is $$ 234.04 + (6)(18.998) = 349.03 \; g/mol \notag $$

   The molar mass of $^{238}UF_6$ is

   $$ 238.05 + (6)(18.998) = 352.04 \; g/mol \notag $$

   The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 10.7.10:

$$\frac{rate\ ^{235}UF_6}{rate\ ^{238}UF_6} = \sqrt{\frac{352.04}{349.03}} = 1.0043$$

Thus passing $UF_6$ containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

2. **B** To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

$$finalpurity = (initialpurity)(separation)^n$$

In this case, 0.990 = (0.00720)(1.0043)$^n$, which can be rearranged to give

$$\frac{0.990}{0.00720} = 1.38 = (1.0043)^n$$

Taking the logarithm of both sides gives

$$log\,(138) = nlog\,(1.0043)$$

$$n = \frac{log\,(138)}{log\,(1.0043)} = 1150 = 1.15 \times 10^3$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched $^{235}U$. Figure 10.7.6 shows a small part of a system that is used to prepare enriched uranium on a large scale.

Exercise

Helium consists of two isotopes: $^3He$ (natural abundance = 0.000134%) and $^4He$ (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant $^4He$ by a process of gaseous effusion.

1. Calculate the ratio of the effusion rates of $^3He$ and $^4He$ and thus the enrichment possible in a single effusion step.
2. How many effusion steps are necessary to yield 99.0% pure $^3He$?

**Answer:** a. ratio of effusion rates = 1.15200; one step gives 0.000154% $^3He$; b. 96 steps

**Figure 10.7.6 A Portion of a Plant for Separating Uranium Isotopes by Effusion of $UF_6$**



*The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous $UF_6$ is pumped through a porous barrier to partially separate the isotopes. The $UF_6$ must be passed through multiple units to become substantially enriched in $^{235}U$.*

## Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have

the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$\overline{KE} = \frac{1}{2}M_1 v_{rms_1}^2 = \frac{1}{2}M_2 v_{rms_2}^2 \tag{10.7.11}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{rms_2}^2}{v_{rms_1}^2} = \frac{M_1}{M_2} \tag{10.7.12}$$

Taking the square root of both sides gives

$$\frac{v_{rms_2}}{v_{rms_1}} = \sqrt{\frac{M_1}{M_2}} \tag{10.7.13}$$

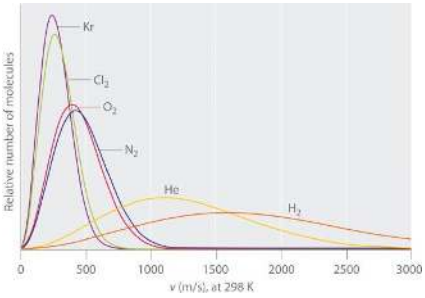
Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 10.7.13 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in Figure 10.7.7 for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds. The postulates of the kinetic molecular theory of gases lead to the following equation, which directly relates molar mass, temperature, and rms speed:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{10.7.14}$$

In this equation, $v_{\text{rms}}$ has units of meters per second; consequently, the units of molar mass $M$ are kilograms per mole, temperature $T$ is expressed in kelvins, and the ideal gas constant $R$ has the value 8.3145 J/(K·mol).

**Figure 10.7.7 The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses**




The lightest gases have a wider distribution of speeds and the highest average speeds.

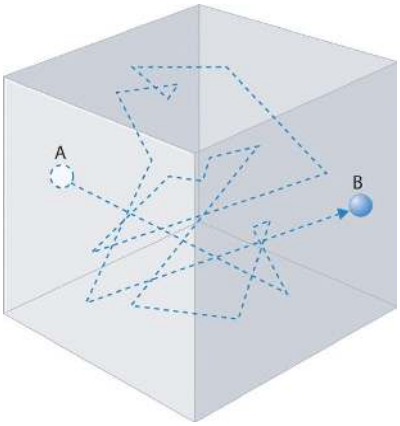
### Note the Pattern

Molecules with lower masses have a wider distribution of speeds and a higher average speed.

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as $10^{10}$ times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in Figure 10.7.8 The average distance traveled by a molecule between collisions is the mean free pathThe average distance traveled by a molecule between collisions.. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C, for example, an oxygen or nitrogen molecule in the atmosphere travels only about $6.0 \times 10^{-8}$ m (60 nm) between collisions. In the

upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as $1 \times 10^{10}$ m (about 6 million miles).

**Figure 10.7.8 The Path of a Single Particle in a Gas Sample**




*The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.*

### Note the Pattern

The denser the gas, the shorter the mean free path.

### Example 10.7.4

Calculate the rms speed of a sample of *cis*-2-butene ($C_4H_8$) at 20°C.

**Given:** compound and temperature

**Asked for:** rms speed

**Strategy:**

Calculate the molar mass of *cis*-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 10.39 to calculate the rms speed of the gas.

**Solution:**

To use Equation 10.7.14, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is $C_4H_8$, so its molar mass is 56.11 g/mol. Thus

$$v_{rms} = \sqrt{\frac{3RT}{M}} \tag{10.7.14}$$

Exercise

Calculate the rms speed of a sample of radon gas at 23°C

$$M = 56.11\ g/mol = 56.11 \times 10^{-3}\ kg/mol$$

$$T = 20 + 273 = 293\ K$$

$$R = 8.3145\ J/\left(K \cdot mol\right) = 8.3145\ \left(kg \cdot m^2\right) / \left(s^2 \cdot K \cdot mol\right)$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \cdot 8.3145\ \left(\cancel{kg} \cdot m^2\right) / \left(s^2 \cdot\ \cancel{K \cdot mol}\right) \cdot 293\ K}{56.11 \times 10^{-3}\ \cancel{kg} / \cancel{mol}}} = 3.61 \times 10^2\ m/s$$

.

**Answer:** $1.82 \times 10^2$ m/s (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not "ideal," although their behavior usually approximates that of an ideal gas. In Chapter 11 we explore how the behavior of real gases differs from that of ideal gases.

## Summary

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed ($v_{rms}$)**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average. **Diffusion** is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham's law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

## Key Takeaway

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.

## Key Equations

**Average kinetic energy**

Equation 10.7.6:

$$\overline{e_K} = \frac{1}{2}m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{10.7.1}$$

**Root mean square speed**

Equation 10.7.8 :

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{10.7.8}$$

**Graham's law for diffusion and effusion**

Equation 10.7.10

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{10.7.10}$$

**Kinetic molecular theory of gases**

Equation 10.7.14:

$$v_{rms} = \sqrt{\frac{3RT}{M}} \tag{10.7.2}$$

## Conceptual Problems

1. Which of the following processes represents effusion, and which represents diffusion?
    1. helium escaping from a hole in a balloon
    2. vapor escaping from the surface of a liquid
    3. gas escaping through a membrane

2. Which postulate of the kinetic molecular theory of gases most readily explains the observation that a helium-filled balloon is round?
3. Why is it relatively easy to compress a gas? How does the compressibility of a gas compare with that of a liquid? A solid? Why? Which of the postulates of the kinetic molecular theory of gases most readily explains these observations?
4. What happens to the average kinetic energy of a gas if the rms speed of its particles increases by a factor of 2? How is the rms speed different from the average speed?
5. Which gas—radon or helium—has a higher average kinetic energy at 100°C? Which has a higher average speed? Why? Which postulate of the kinetic molecular theory of gases most readily supports your answer?
6. What is the relationship between the average speed of a gas particle and the temperature of the gas? What happens to the distribution of molecular speeds if the temperature of a gas is increased? Decreased?
7. Qualitatively explain the relationship between the number of collisions of gas particles with the walls of a container and the pressure of a gas. How does increasing the temperature affect the number of collisions?
8. What happens to the average kinetic energy of a gas at constant temperature if the
    1. volume of the gas is increased?
    2. pressure of the gas is increased?
9. What happens to the density of a gas at constant temperature if the
    1. volume of the gas is increased?
    2. pressure of the gas is increased?
10. Use the kinetic molecular theory of gases to describe how a decrease in volume produces an increase in pressure at constant temperature. Similarly, explain how a decrease in temperature leads to a decrease in volume at constant pressure.
11. Graham's law is valid only if the two gases are at the same temperature. Why?
12. If we lived in a helium atmosphere rather than in air, would we detect odors more or less rapidly than we do now? Explain your reasoning. Would we detect odors more or less rapidly at sea level or at high altitude? Why?

## Numerical Problems

1. At a given temperature, what is the ratio of the rms speed of the atoms of Ar gas to the rms speed of molecules of $H_2$ gas?
2. At a given temperature, what is the ratio of the rms speed of molecules of CO gas to the rms speed of molecules of $H_2S$ gas?
3. What is the ratio of the rms speeds of argon and oxygen at any temperature? Which diffuses more rapidly?
4. What is the ratio of the rms speeds of Kr and NO at any temperature? Which diffuses more rapidly?
5. Deuterium (D) and tritium (T) are heavy isotopes of hydrogen. Tritium has an atomic mass of 3.016 amu and has a natural abundance of 0.000138%. The effusion of hydrogen gas (containing a mixture of $H_2$, HD, and HT molecules) through a porous membrane can be used to obtain samples of hydrogen that are enriched in tritium. How many membrane passes are necessary to give a sample of hydrogen gas in which 1% of the hydrogen molecules are HT?
6. Samples of HBr gas and $NH_3$ gas are placed at opposite ends of a 1 m tube. If the two gases are allowed to diffuse through the tube toward one another, at what distance from each end of the tube will the gases meet and form solid $NH_4Br$?

## Answer

1. At any temperature, the rms speed of hydrogen is 4.45 times that of argon.
2. 
3. 
4. 
5. 
6. 

## Contributors

- Anonymous

Modified by Joshua Halpern

Figure 10.7.3 by the Backyard Scientist @ YouTube

Figure 10.7.4 frrom NCSSMDistance Ed @ YouTube

Tumbnail from Wikimedia

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# 10.8: Real Gases

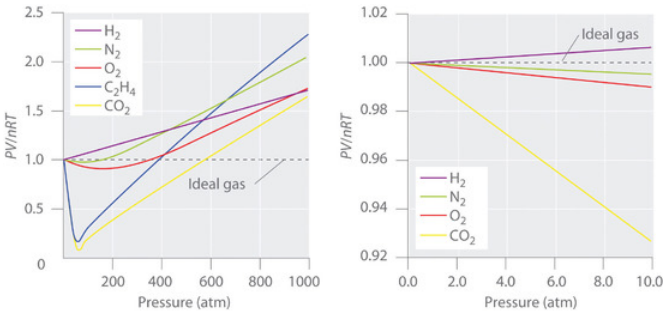
**Learning Objectives**

- To recognize the differences between the behavior of an ideal gas and a real gas.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

## Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of *PV*/*nRT* versus *P* gives a horizontal line with an intercept of 1 on the *PV*/*nRT* axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (part (a) in Figure 11.1.1 ). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure 11.1.1 ). Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 11.1.2 for $N_2$. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.




(a) *PV*/*nRT* at high pressures (b) *PV*/*nRT* at low pressures

Figure 11.1.1 Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures (a) In these plots of *PV*/*nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for $C_2H_4$ and $CO_2$ because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

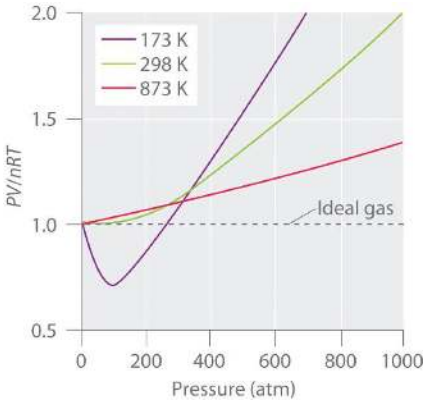



Figure 11.1.2 The Effect of Temperature on the Behavior of Real Gases A plot of *PV*/*nRT* versus *P* for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures,

the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 11.1.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.

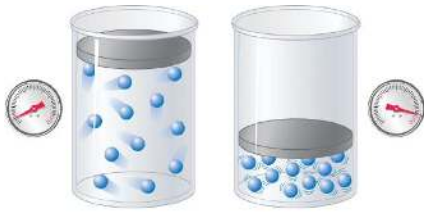



Figure 11.1.3 The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 11.1.3). Thus as shown in Figure 11.1.2, at low temperatures, the ratio of *PV*/*nRT* is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the *PV*/*nRT* versus *P* plot for many gases.

### Note the Pattern

Nonzero molecular volume makes the actual volume *greater* than predicted at high pressures; intermolecular attractions make the pressure *less* than predicted.

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

## The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called van der Waals equationA modification of the ideal gas law designed to describe the behavior of real gases by explicitly including the effects of molecular volume and intermolecular forces., 

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{11.1.1}$$

*a* and *b* are empirical constants that are different for each gas. The values of *a* and *b* are listed in Table 11.1.5 for several common gases. The pressure term $P + (an^2/V^2)$ corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, $n^2/V^2$ represents the concentration of the gas ($n/V$) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure 10.1.4 . The volume term $V - nb$ corrects for the volume occupied by the gaseous molecules.

**Table 11.1.1 van der Waals Constants for Some Common Gases**

| Gas | $a$ ($L^2$·atm)/$mol^2$) | $b$ (L/mol) |
|---|---|---|
| He | 0.03410 | 0.0238 |
| Ne | 0.205 | 0.0167 |
| Ar | 1.337 | 0.032 |
| $H_2$ | 0.2420 | 0.0265 |
| $N_2$ | 1.352 | 0.0387 |
| $O_2$ | 1.364 | 0.0319 |
| $Cl_2$ | 6.260 | 0.0542 |
| $NH_3$ | 4.170 | 0.0371 |
| $CH_4$ | 2.273 | 0.0430 |
| $CO_2$ | 3.610 | 0.0429 |

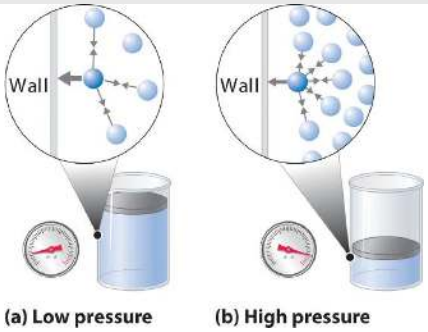



Figure 11.1.4 The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on $V$ and $P$, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the $an^2/V^2$ term must be added to the measured pressure to correct for these effects.

### Example 11.1.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.0 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

**Given:** volume of cylinder, mass of compound, pressure, and temperature

**Asked for:** safety

**Strategy:**

**A** Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

**B** Obtain *a* and *b* values for $Cl_2$ from Table 11.1.1 . Use the van der Waals equation to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

**Solution:**

**A** We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$\left(500 \cancel{g}\right)\left(\frac{1\ mol}{70.906\ \cancel{g}} = 7.05 mol\ Cl_2\right)$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{\left(7.05\ \cancel{mol}\right)\left[0.08206\left(\cancel{L}\cdot atm\right)/\left(\cancel{K}\cdot\cancel{mol}\right)\right]\left(298\ \cancel{K}\right)}{4.0\ \cancel{L}} = 43\ atm$$

If chlorine behaves like an ideal gas, you have a real problem!

**B** Now let's use the van der Waals equation with the *a* and *b* values for $Cl_2$ from Table 11.1.1 . Solving for *P* gives

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$= \frac{\left(7.05\ \cancel{mol}\right)\left[0.08206\left(\cancel{L}\cdot atm\right)/\left(\cancel{K}\cdot\cancel{mol}\right)\right]\left(298\ \cancel{K}\right)}{4.0\ \cancel{L} - 7.05\ \cancel{mol}\left(0.0542\ \cancel{L}/\cancel{mol}\right)} - \frac{6.260^2\ \cancel{L^2}\cdot atm/\cancel{mol^2}\left(7.05\ \cancel{mol^2}\right)}{4.0\ \cancel{L^2}}$$

$$= 47.7\ atm - 19.4\ atm = 28\ atm\ (2\ significant\ figures)$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

1. ideal gas law.
2. van der Waals equation.

**Answer:** a. 77 atm; b. 67 atm

## Liquefaction of Gases

LiquefactionThe condensation of gases into a liquid form. of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals *a* coefficients are relatively easy to liquefy because large *a* coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small *a* coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate $O_2$, $N_2$, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points. In Chapter 11.2 , we will consider in more detail the nature of the intermolecular forces that allow gases to liquefy.

### Note the Pattern

A large value of *a* indicates the presence of relatively strong intermolecular attractive interactions.

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids (an ultracold liquid formed from the liquefaction of gases., from the Greek *kryo*, meaning "cold," and *genes*, meaning "producing"). They have applications as

refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure 11.1.5 A Liquid Natural Gas Transport Ship

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 11.1.5 ). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

## Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of *PV*/*nRT* versus *P* at a given temperature; for an ideal gas, *PV*/*nRT* versus *P* = 1 under all conditions. At high pressures, most real gases exhibit larger *PV*/*nRT* values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit *PV*/*nRT* values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

## Key Takeaway

- Molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

## Key Equation

**van der Waals equation**

Equation 11.1.1: $\left(p + \frac{an^2}{V^2}\right)(V - b) = nRT$<mi/>

## Conceptual Problems

1. What factors cause deviations from ideal gas behavior? Use a sketch to explain your answer based on interactions at the molecular level.
2. Explain the effect of nonzero atomic volume on the ideal gas law at high pressure. Draw a typical graph of volume versus 1/*P* for an ideal gas and a real gas.
3. For an ideal gas, the product of pressure and volume should be constant, regardless of the pressure. Experimental data for methane, however, show that the value of *PV* decreases significantly over the pressure range 0 to 120 atm at 0°C. The decrease in *PV* over the same pressure range is much smaller at 100°C. Explain why *PV* decreases with increasing temperature. Why is the decrease less significant at higher temperatures.
4. What is the effect of intermolecular forces on the liquefaction of a gas? At constant pressure and volume, does it become easier or harder to liquefy a gas as its temperature increases? Explain your reasoning. What is the effect of increasing the pressure on the liquefaction temperature?

5. Describe qualitatively what *a* and *b*, the two empirical constants in the van der Waals equation, represent.
6. In the van der Waals equation, why is the term that corrects for volume negative and the term that corrects for pressure positive? Why is $n/V$ squared?
7. Liquefaction of a gas depends strongly on two factors. What are they? As temperature is decreased, which gas will liquefy first—ammonia, methane, or carbon monoxide? Why?
8. What is a cryogenic liquid? Describe three uses of cryogenic liquids.
9. Air consists primarily of $O_2$, $N_2$, Ar, Ne, Kr, and Xe. Use the concepts discussed in this chapter to propose two methods by which air can be separated into its components. Which component of air will be isolated first?
10. How can gas liquefaction facilitate the storage and transport of fossil fuels? What are potential drawbacks to these methods?

## Numerical Problems

1. The van der Waals constants for xenon are $a = 4.19\ (L^2{\cdot}atm)/mol^2$ and $b = 0.0510$ L/mol. If a 0.250 mol sample of xenon in a container with a volume of 3.65 L is cooled to −90°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?
2. The van der Waals constants for water vapor are $a = 5.46\ (L^2{\cdot}atm)/mol^2$ and $b = 0.0305$ L/mol. If a 20.0 g sample of water in a container with a volume of 5.0 L is heated to 120°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

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# 10.9: Essential Skills 5

**Learning Objectives**

- Natural Logarithms
- Calculations Using Natural Logarithms

Essential Skills 3 in Section 4.11, introduced the common, or base-10, logarithms and showed how to use the properties of exponents to perform logarithmic calculations. In this section, we describe natural logarithms, their relationship to common logarithms, and how to do calculations with them using the same properties of exponents.

## Natural Logarithms

Many natural phenomena exhibit an exponential rate of increase or decrease. Population growth is an example of an exponential rate of increase, whereas a runner's performance may show an exponential decline if initial improvements are substantially greater than those that occur at later stages of training. Exponential changes are represented logarithmically by $e^x$, where $e$ is an irrational number whose value is approximately 2.7183. The *natural logarithm*, abbreviated as ln, is the power $x$ to which $e$ must be raised to obtain a particular number. The natural logarithm of $e$ is 1 ($\ln e = 1$).

Some important relationships between base-10 logarithms and natural logarithms are as follows:

$10^1 = 10 = e^{2.303}$ $\ln e^x = x \ln 10 = \ln(e^{2.303}) = 2.303 \log 10 = \ln e = 1$

According to these relationships, $\ln 10 = 2.303$ and $\log 10 = 1$. Because multiplying by 1 does not change an equality,

$\ln 10 = 2.303 \log 10$

Substituting any value $y$ for 10 gives

$\ln y = 2.303 \log y$

Other important relationships are as follows:

$\log A^x = x \log A$ $\ln e^x = x \ln e = x = e^{\ln x}$

Entering a value $x$, such as 3.86, into your calculator and pressing the "ln" key gives the value of $\ln x$, which is 1.35 for $x = 3.86$. Conversely, entering the value 1.35 and pressing "$e^x$" key gives an answer of 3.86.On some calculators, pressing [INV] and then [ln $x$] is equivalent to pressing [$ex$]. Hence

$e^{\ln 3.86} = e^{1.35} = 3.86$ $\ln(e^{3.86}) = 3.86$

### Skill Builder ES1

Calculate the natural logarithm of each number and express each as a power of the base $e$.

1. 0.523
2. 1.63

**Solution:**

1. $\ln(0.523) = -0.648$; $e^{-0.648} = 0.523$
2. $\ln(1.63) = 0.489$; $e^{0.489} = 1.63$

### Skill Builder ES2

What number is each value the natural logarithm of?

1. 2.87
2. 0.030
3. −1.39

**Solution:**

1. $\ln x = 2.87$; $x = e^{2.87} = 17.6 = 18$ to two significant figures

2. ln $x$ = 0.030; $x = e^{0.030}$ = 1.03 = 1.0 to two significant figures
3. ln $x$ = −1.39; $x = e^{-1.39}$ = 0.249 = 0.25

## Calculations with Natural Logarithms

Like common logarithms, natural logarithms use the properties of exponents. We can compare the properties of common and natural logarithms:

| Operation | Exponential Form | Logarithm |
|---|---|---|
| Multiplication | $(10^a)(10^b) = 10^{a+b}$ | $\log(ab) = \log a + \log b$ |
| | $(e^x)(e^y) = e^{x+y}$ | $\ln(e^x e^y) = \ln(e^x) + \ln(e^y) = x + y$ |
| Division | $\frac{10^a}{10^b} = 10^{a-b}$<br>$\frac{e^a}{e^b} = e^{a-b}$ | $log\left(\frac{a}{b}\right) = log\ a - log\ b$<br>$ln\left(\frac{x}{y}\right) = ln\ x - ln\ y$<br>$ln\left(\frac{e^x}{e^y}\right) = ln\,(e^x) - ln\,(e^y) = x - y$ |
| Inverse | | $log\left(\frac{1}{a}\right) = -log\,(a)$<br>$ln\left(\frac{1}{x}\right) = -ln\,(x)$ |

The number of significant figures in a number is the same as the number of digits after the decimal point in its logarithm. For example, the natural logarithm of 18.45 is 2.9151, which means that $e^{2.9151}$ is equal to 18.45.

### Skill Builder ES3

Calculate the natural logarithm of each number.

1. 22 × 18.6
2. $\frac{0.51}{2.67}$
3. 0.079 × 1.485
4. $\frac{20.5}{0.026}$

**Solution:**

1. ln(22 × 18.6) = ln(22) + ln(18.6) = 3.09 + 2.923 = 6.01. Alternatively, 22 × 18.6 = 410; ln(410) = 6.02.
2. $ln\left(\frac{0.51}{2.67}\right) = ln\,(0.51) - ln\,(2.67) = -0.67 - 0.982 = -1.65$ ln(0.19) = −1.66.
3. ln(0.079 × 1.485) = ln(0.079) + ln(1.485) = −2.54 + 0.395 = −2.15. Alternatively, 0.079 × 1.485 = 0.12; ln(0.12) = −2.12.
4. $ln\left(\frac{20.5}{0.026}\right) = ln\,(20.5) - ln\,(0.026) = 3.0204 - (-3.65) = 6.67$ ln(790) = 6.67.

The answers obtained using the two methods may differ slightly due to rounding errors.

### Skill Builder ES4

Calculate the natural logarithm of each number.

1. 34 × 16.5
2. 2.10/0.052
3. 0.402 × 3.930

4. 0.164/10.7

**Solution:**

1. 6.33
2. 3.70
3. 0.457
4. −4.178

## Contributors

- Anonymous

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# CHAPTER OVERVIEW

## 11: Fluids


11.1: Introduction
11.2: Intermolecular forces
11.3: Unique Properties of Liquids
11.4: Vapor Pressure
11.5: Changes of State
11.6: Critical Temperature and Pressure
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# 11.1: Introduction

**Learning Objectives**

- To be familiar with the kinetic molecular description of liquids.

The kinetic molecular theory of gases described in Chapter 10 gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

## Density

The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore more commonly measured in units of grams per cubic centimeter ($g/cm^3$) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.

## Molecular Order

Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids discussed in Section 4.1, the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.

## Compressibility

Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.

## Thermal Expansion

The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table 11.0.1 that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

**Table 11.0.1 The Density of Water at Various Temperatures**

| T (°C) | Density ($g/cm^3$) |
|---|---|
| 0 | 0.99984 |
| 30 | 0.99565 |
| 60 | 0.98320 |
| 90 | 0.96535 |

## Diffusion

Molecules in fluids diffuse because they are in constant motion (Figure 11.0.1). A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower

than in gases.



**ɛcular Diffusion in a Liquid** A drop of an aqueous solution containing a marker dye is added to a larger volume ses, the color of the dye becomes fainter at the edges.

## Fluidity

Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 11.0.2 ).

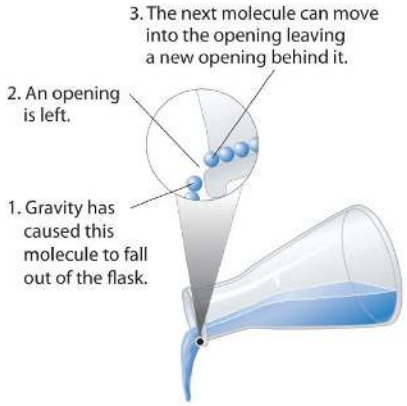



Figure 11.0.2 Why Liquids Flow Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container.

## Summary

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described in Chapter 10 . This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers.

## Key Takeaway

- The kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

## Conceptual Problems

1. A liquid, unlike a gas, is virtually *incompressible*. Explain what this means using macroscopic and microscopic descriptions. What general physical properties do liquids share with solids? What properties do liquids share with gases?
2. Using a kinetic molecular approach, discuss the differences and similarities between liquids and gases with regard to
    1. thermal expansion.
    2. fluidity.
    3. diffusion.
3. How must the ideal gas law be altered to apply the kinetic molecular theory of gases to liquids? Explain.
4. Why are the root mean square speeds of molecules in liquids less than the root mean square speeds of molecules in gases?

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# 11.2: Intermolecular forces

**Learning Objectives**

- Explain the following laws within the Ideal Gas Law

The properties of liquids are intermediate between those of gases and solids but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

### Note the Pattern

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law, see Section 7.1.)

In this section, we explicitly consider three kinds of intermolecular interactions:There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. (For more information on ionic bonding, see Chapter 4. For more information on the dissolution of ionic substances, see Chapter 9) *dipole–dipole interactions*, *London dispersion forces*, and *hydrogen bonds*. The first two are often described collectively as van der Waals forcesThe intermolecular forces known as dipole–dipole interactions and London dispersion forces..

## Dipole–Dipole Interactions

Recall from Chapter 4 that polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 11.2.1 . These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 11.2.1). Hence dipole–dipole interactionsA kind of intermolecular interaction (force) that results between molecules with net dipole moments., such as those in part (b) in Figure 11.2.1 , are *attractive intermolecular interactions*, whereas those in part (d) in Figure 11.2.1 are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 11.2.2 . On average, however, the attractive interactions dominate.

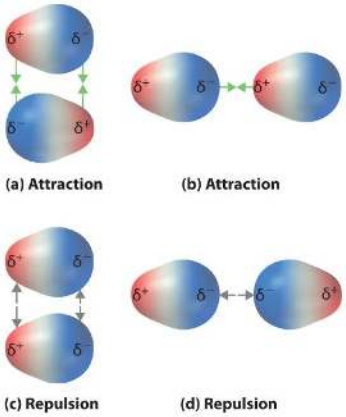



Figure 11.2.1 Attractive and Repulsive Dipole–Dipole Interactions (a and b) Molecular orientations in which the positive end of one dipole ($\delta^+$) is near the negative end of another ($\delta^-$) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

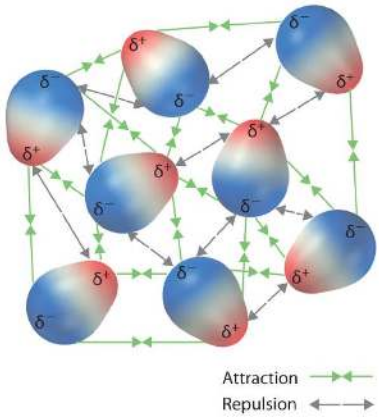



**Figure 11.2.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules**

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions we considered in Chapter 4 . Recall that the attractive energy between two ions is proportional to $1/r$, where $r$ is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by $2^6$, or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 11.2.1 . Using what we learned in Chapter 5 about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

**Table 11.2.1 Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass**

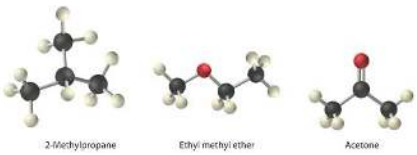
| Compound | Molar Mass (g/mol) | Dipole Moment (D) | Boiling Point (K) |
|---|---|---|---|
| $C_3H_6$ (cyclopropane) | 42 | 0 | 240 |
| $CH_3OCH_3$ (dimethyl ether) | 46 | 1.30 | 248 |
| $CH_3CN$ (acetonitrile) | 41 | 3.9 | 355 |

### Note the Pattern

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

### Example 11.2.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone ($CH_3COCH_3$) in order of increasing boiling points. Their structures are as follows:




**Given:** compounds

**Asked for:** order of increasing boiling points

**Strategy:**

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

**Solution:**

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to $H_2O$; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise

Arrange carbon tetrafluoride ($CF_4$), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

**Answer:** dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

## London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 11.2.2 )

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole momentsThe short-lived dipole moment in atoms and nonpolar molecules caused by the constant motion of their electrons, which results in an asymmetrical distribution of charge at any given instant., which produce attractive forces called London dispersion

forcesA kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules. between otherwise nonpolar substances.

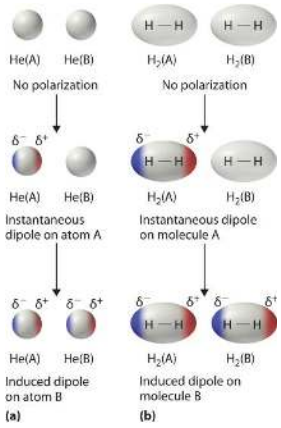



Figure 11.2.3 Instantaneous Dipole Moments The formation of an instantaneous dipole moment on one He atom (a) or an $H_2$ molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

**Table 11.2.2 Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds**

| Substance | Molar Mass (g/mol) | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|
| Ar | 40 | −189.4 | −185.9 |
| Xe | 131 | −111.8 | −108.1 |
| $N_2$ | 28 | −210 | −195.8 |
| $O_2$ | 32 | −218.8 | −183.0 |
| $F_2$ | 38 | −219.7 | −188.1 |
| $I_2$ | 254 | 113.7 | 184.4 |
| $CH_4$ | 16 | −182.5 | −161.5 |

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 11.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipoleA short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment., in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by $2^6$, or 64-fold.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two $H_2$ molecules in part (b) in Figure 11.2.3 tends to become more pronounced as atomic and molecular masses increase (Table 11.2.2 ). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. (For more information on shielding, see Section 2.2) As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution

in an atom or molecule is called its polarizabilityThe ease of deformation of the electron distribution in an atom or molecule.. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

### Note the Pattern

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles, as we shall see when we discuss solutions in Chapter 13. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 11.2.4 ). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 11.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula $C_5H_{12}$. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

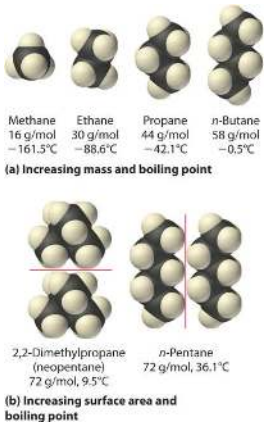



Figure 11.2.4 Mass and Surface Area Affect the Strength of London Dispersion Forces (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

### Example 11.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

**Given:** compounds

**Asked for:** order of increasing boiling points

**Strategy:**

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

**Solution:**

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to

its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise

Arrange $GeH_4$, $SiCl_4$, $SiH_4$, $CH_4$, and $GeCl_4$ in order of decreasing boiling points.

**Answer:** $GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > $GeH_4$ (−88.5°C) > $SiH_4$ (−111.8°C) > $CH_4$ (−161°C)

## Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 11.2.5 . Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for $H_2Te$ and $H_2Se$ to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

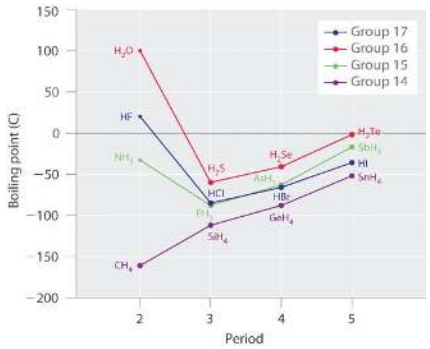



Figure 11.2.5 The Effects of Hydrogen Bonding on Boiling Points These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, $NH_3$, and $H_2O$) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bondsAn unusually strong dipole-dipole interaction (intermolecular force) that results when hydrogen is bonded to very electronegative elements, such as O, N, and F., as shown for ice in Figure 11.2.6 . A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O·H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

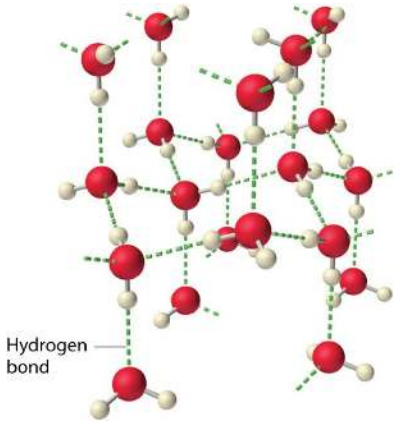



Figure 11.2.6 The Hydrogen-Bonded Structure of Ice Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

### Note the Pattern

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by "antifreeze" (we will discuss how antifreeze works in Chapter 13) and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid $NH_3$. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

### Example 11.2.3

Considering $CH_3OH$, $C_2H_6$, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

**Given:** compounds

**Asked for:** formation of hydrogen bonds and structure

**Strategy:**

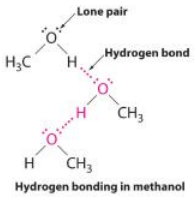
**A** Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

**B** Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

**Solution:**

**A** Of the species listed, xenon (Xe), ethane ($C_2H_6$), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

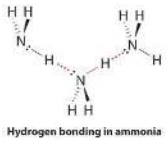
**B** The one compound that can act as a hydrogen bond donor, methanol ($CH_3OH$), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:

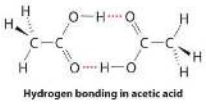



Exercise

Considering $CH_3CO_2H$, $(CH_3)_3N$, $NH_3$, and $CH_3F$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

**Answer:** $CH_3CO_2H$ and $NH_3$;




## Example 11.2.4

Arrange $C_{60}$ (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and $N_2O$ in order of increasing boiling points.

**Given:** compounds

**Asked for:** order of increasing boiling points

**Strategy:**

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

**Solution:**

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and $N_2O$ have very similar molar masses (40 and 44 g/mol, respectively), but $N_2O$ is polar while Ar is not. Consequently, $N_2O$ should have a higher boiling point. A $C_{60}$ molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or $N_2O$. Because the boiling points of nonpolar substances increase rapidly with molecular mass, $C_{60}$ should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (−269°C) < Ar (−185.7°C) < $N_2O$ (−88.5°C) < $C_{60}$ (>280°C) < NaCl (1465°C).

Exercise

Arrange 2,4-dimethylheptane, Ne, $CS_2$, $Cl_2$, and KBr in order of decreasing boiling points.

**Answer:** KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > $CS_2$ (46.6°C) > $Cl_2$ (−34.6°C) > Ne (−246°C)

## Summary

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where $r$ is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons

are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O·H> hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

### Key Takeaway

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

### Conceptual Problems

1. What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?
2. Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.
3. Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.
4. Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?
5. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
6. Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.
7. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
8. Using acetic acid as an example, illustrate both attractive and repulsive intermolecular interactions. How does the boiling point of a substance depend on the magnitude of the repulsive intermolecular interactions?
9. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
10. The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, −85°C; HBr, −67°C; and HI, −34°C. Explain any trends in the data, as well as any deviations from that trend.
11. Identify the most important intermolecular interaction in each of the following.
    1. $SO_2$
    2. HF
    3. $CO_2$
    4. $CCl_4$
    5. $CH_2Cl_2$
12. Identify the most important intermolecular interaction in each of the following.
    1. LiF
    2. $I_2$
    3. ICl
    4. $NH_3$
    5. $NH_2Cl$
13. Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)
14. Arrange Kr, $Cl_2$, $H_2$, $N_2$, Ne, and $O_2$ in order of increasing polarizability. Explain your reasoning.

15. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.
16. The structures of ethanol, ethylene glycol, and glycerin are as follows:

    Arrange these compounds in order of increasing boiling point. Explain your rationale.
17. Do you expect the boiling point of $H_2S$ to be higher or lower than that of $H_2O$? Justify your answer.
18. Ammonia ($NH_3$), methylamine ($CH_3NH_2$), and ethylamine ($CH_3CH_2NH_2$) are gases at room temperature, while propylamine ($CH_3CH_2CH_2NH_2$) is a liquid at room temperature. Explain these observations.
19. Why is it not advisable to freeze a sealed glass bottle that is completely filled with water? Use both macroscopic and microscopic models to explain your answer. Is a similar consideration required for a bottle containing pure ethanol? Why or why not?
20. Which compound in the following pairs will have the higher boiling point? Explain your reasoning.
    1. $NH_3$ or $PH_3$
    2. ethylene glycol ($HOCH_2CH_2OH$) or ethanol
    3. 2,2-dimethylpropanol [$CH_3C(CH_3)_2CH_2OH$] or *n*-butanol ($CH_3CH_2CH_2CH_2OH$)
21. Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?
22. Use the melting of a metal such as lead to explain the process of melting in terms of what is happening at the molecular level. As a piece of lead melts, the temperature of the metal remains constant, even though energy is being added continuously. Why?
23. How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the $H_2O$ molecule? What effect does this have on the structure and density of ice?
24. 1. Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular <math display="inline" xml:id="av_1.0-ch11_m003"><semantics><mrow><mtext>H</mtext><mo>·</mo><mo>·</mo><mo>·</mo><mtext>I</mtext></mrow></semantics></math> interactions in liquid HI.
    2. In which substance are the individual hydrogen bonds stronger: HF or $H_2O$? Explain your reasoning.
    3. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or $H_2O$? Explain your reasoning.

## Answers

1.
2.
3.
4.
5. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.
6.
7.
8.
9. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure.
10.

11. 1. The V-shaped $SO_2$ molecule has a large dipole moment due to the polar S=O bonds, so dipole–dipole interactions will be most important.
    2. The H–F bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.
    3. Although the C=O bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.
    4. This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.
    5. This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.
12.
13.
14.
15. Water has two polar O–H bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of *four* hydrogen bonds per $H_2O$ molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors, it only has one O–H bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form *two* hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.
16.
17.
18.
19.
20.
21. Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.
22.
23.
24.

## Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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# 11.3: Unique Properties of Liquids

**Learning Objectives**

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions: surface tension, capillary action, and viscosity.

## Surface Tension

We stated in Section 11.0 that liquids tend to adopt the shapes of their containers. Why, then, do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces.

Figure 11.3.1 presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads (see the chapter opener photo). A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

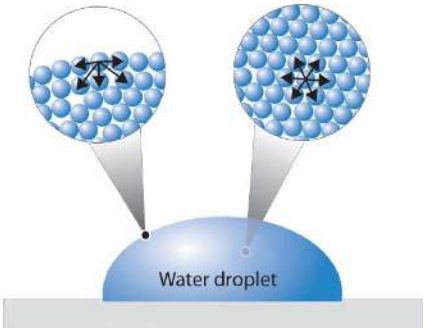


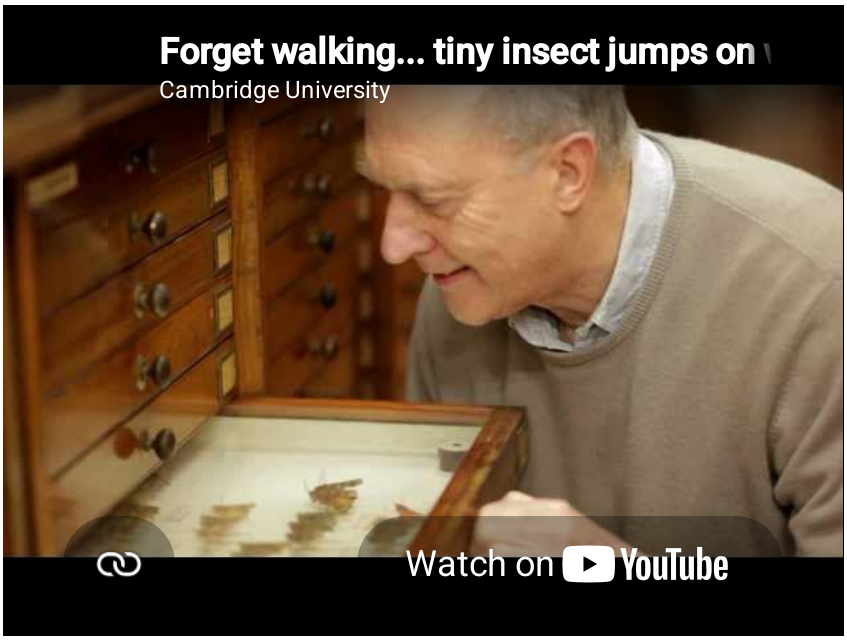

Figure 11.3.1 A Representation of Surface Tension in a Liquid Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces..

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it "floats," even though steel is much denser than water (part (a) in Figure 11.3.2 ). Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking (part (b) in Figure 11.3.2).





**Figure 11.3.2 The Effects of the High Surface Tension of Liquid Water** (a) A paper clip can “float” on water because of surface tension (from Christopher Rozitis.






(b) Surface tension also allows insects such as this water strider to “walk on water.”

Such phenomena are manifestations of surface tensionThe energy required to increase the surface area of a liquid by a certain amount. Surface tension is measured in units of energy per area (e.g., $J/m^2$ )., which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per

square meter ($J/m^2$) or dyne per centimeter (dyn/cm), where 1 dyn = $1 \times 10^{-5}$ N. The values of the surface tension of some representative liquids are listed in Table 11.3.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding, which we will discuss in more detail in Chapter 12.

**Table 11.3.1 Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids**

| Substance | Surface Tension ($\times 10^{-3}$ $J/m^2$) | Viscosity (mPa·s) | Vapor Pressure (mmHg) | Normal Boiling Point (°C) |
|---|---|---|---|---|
| **Organic Compounds** | | | | |
| diethyl ether | 17 | 0.22 | 531 | 34.6 |
| *n*-hexane | 18 | 0.30 | 149 | 68.7 |
| acetone | 23 | 0.31 | 227 | 56.5 |
| ethanol | 22 | 1.07 | 59 | 78.3 |
| ethylene glycol | 48 | 16.1 | ~0.08 | 198.9 |
| **Liquid Elements** | | | | |
| bromine | 41 | 0.94 | 218 | 58.8 |
| mercury | 486 | 1.53 | 0.0020 | 357 |
| **Water** | | | | |
| 0°C | 75.6 | 1.79 | 4.6 | — |
| 20°C | 72.8 | 1.00 | 17.5 | — |
| 60°C | 66.2 | 0.47 | 149 | — |
| 100°C | 58.9 | 0.28 | 760 | — |

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactantsSubstances (surface-active agents), such as soaps and detergents, that disrupt the attractive intermolecular interactions between molecules of a polar liquid, thereby reducing the surface tension of the liquid.. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

## Capillary Action

Intermolecular forces also cause a phenomenon called capillary actionThe tendency of a polar liquid to rise against gravity into a small-diameter glass tube., which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 11.3.3 . When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.






**Figure 11.3.3 The Phenomenon of Capillary Action** When a capillary is placed in liquid ink the ink rises up into the capillary. The smaller the diameter of the capillary, the higher the water rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

Of course, you can see the same phenomina in anything with narrow channels, like bricks






**Figure 11.3.4 The Phenomenon of Capillary Action:** Water rises through a brick in a time lapse video

Capillary action is the net result of two opposing sets of forces: cohesive forcesThe intermolecular forces that hold a liquid together., which are the intermolecular forces that hold a liquid together, and adhesive forcesThe attractive intermolecular forces between a liquid and the substance comprising the surface of a capillary., which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure 11.3.5 ). The upper surface of a liquid in a tube is called the meniscusThe upper surface of the liquid in a tube., and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (part (b) in Figure 11.3.5 ).

### Note the Pattern

Polar substances are drawn up a glass capillary and generally have a concave meniscus.

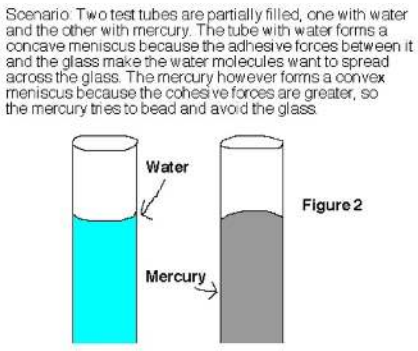
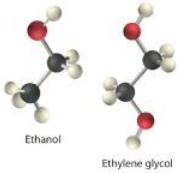



Figure 11.3.5 The Effects of Capillary Action This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is *lower* than the level of the liquid outside the tube. Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

## Viscosity




Viscosity (η)The resistance of a liquid to flow. is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa·s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 10.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

### Note the Pattern

Viscosity increases as intermolecular interactions or molecular size increases.

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic

energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures. The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity. So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

### Example 11.3.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

**Given:** substance and composition of the glass surface

**Asked for:** behavior of oil and the shape of meniscus

**Strategy:**

**A** Identify the cohesive forces in the motor oil.

**B** Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

**Solution:**

**A** Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains. **B** Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

**Answer:** Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

### Summary

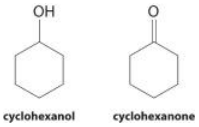
**Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

### Key Takeaway

- Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions.

## Conceptual Problems

1. Why is a water droplet round?
2. How is the environment of molecules on the surface of a liquid droplet different from that of molecules in the interior of the droplet? How is this difference related to the concept of surface tension?
3. Explain the role of intermolecular and intramolecular forces in surface tension.
4. A mosquito is able to walk across water without sinking, but if a few drops of detergent are added to the water, the insect will sink. Why?
5. Explain how soaps or surfactants decrease the surface tension of a liquid. How does the meniscus of an aqueous solution in a capillary change if a surfactant is added? Illustrate your answer with a diagram.
6. Of $CH_2Cl_2$, hexane, and ethanol, which has the lowest viscosity? Which has the highest surface tension? Explain your reasoning in each case.
7. At 25°C, cyclohexanol has a surface tension of 32.92 $mN/m^2$, whereas the surface tension of cyclohexanone, which is very similar chemically, is only 25.45 $mN/m^2$. Why is the surface tension of cyclohexanone so much less than that of cyclohexanol?

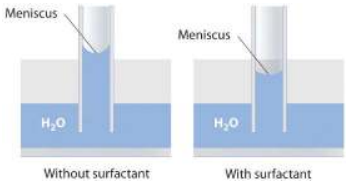



8. What is the relationship between
    1. surface tension and temperature?
    2. viscosity and temperature?

    Explain your answers in terms of a microscopic picture.
9. What two opposing forces are responsible for capillary action? How do these forces determine the shape of the meniscus?
10. Which of the following liquids will have a concave meniscus in a glass capillary? Explain your reasoning.
    1. pentane
    2. diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$)
    3. carbon tetrachloride
11. How does viscosity depend on molecular shape? What molecular features make liquids highly viscous?

## Answers

1.
2.
3.
4.
5. Adding a soap or a surfactant to water disrupts the attractive intermolecular interactions between water molecules, thereby decreasing the surface tension. Because water is a polar molecule, one would expect that a soap or a surfactant would also disrupt the attractive interactions responsible for adhesion of water to the surface of a glass capillary. As shown in the sketch, this would decrease the height of the water column inside the capillary, as well as making the meniscus less concave.




6.

7. As the structures indicate, cyclohexanol is a polar substance that can engage in hydrogen bonding, much like methanol or ethanol; consequently, it is expected to have a higher surface tension due to stronger intermolecular interactions.
8. 
9. Cohesive forces are the intermolecular forces that hold the molecules of the liquid together, while adhesive forces are the attractive forces between the molecules of the liquid and the walls of the capillary. If the adhesive forces are stronger than the cohesive forces, the liquid is pulled up into the capillary and the meniscus is concave. Conversely, if the cohesive forces are stronger than the adhesive forces, the level of the liquid inside the capillary will be lower than the level outside the capillary, and the meniscus will be convex.
10. 
11. Viscous substances often consist of molecules that are much longer than they are wide and whose structures are often rather flexible. As a result, the molecules tend to become tangled with one another (much like overcooked spaghetti), which decreases the rate at which they can move through the liquid.

## Numerical Problems

1. The viscosities of five liquids at 25°C are given in the following table. Explain the observed trends in viscosity.

| Compound | Molecular Formula | Viscosity (mPa·s) |
|---|---|---|
| benzene | $C_6H_6$ | 0.604 |
| aniline | $C_6H_5NH_2$ | 3.847 |
| 1,2-dichloroethane | $C_2H_4Cl_2$ | 0.779 |
| heptane | $C_7H_{16}$ | 0.357 |
| 1-heptanol | $C_7H_{15}OH$ | 5.810 |

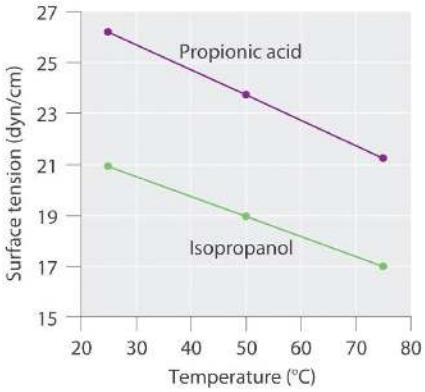
2. The following table gives values for the viscosity, boiling point, and surface tension of four substances. Examine these data carefully to see whether the data for each compound are internally consistent and point out any obvious errors or inconsistencies. Explain your reasoning.

| Compound | Viscosity (mPa·s at 20°C) | Boiling Point (°C) | Surface Tension (dyn/cm at 25°C) |
|---|---|---|---|
| A | 0.41 | 61 | 27.16 |
| B | 0.55 | 65 | 22.55 |
| C | 0.92 | 105 | 36.76 |
| D | 0.59 | 110 | 28.53 |

3. Surface tension data (in dyn/cm) for propanoic acid ($C_3H_6O_2$), and 2-propanol ($C_3H_8O$), as a function of temperature, are given in the following table. Plot the data for each compound and explain the differences between the two graphs. Based on these data, which molecule is more polar?

| Compound | 25°C | 50°C | 75°C |
|---|---|---|---|
| propanoic acid | 26.20 | 23.72 | 21.23 |
| 2-propanol | 20.93 | 18.96 | 16.98 |

## Answer

1.
2.
3. 


   The plots of surface tension versus temperature for propionic acid and isopropanol have essentially the same slope, but at all temperatures the surface tension of propionic acid is about 30% greater than for isopropanol. Because surface tension is a measure of the cohesive forces in a liquid, these data suggest that the cohesive forces for propionic acid are significantly greater than for isopropanol. Both substances consist of polar molecules with similar molecular masses, and the most important intermolecular interactions are likely to be dipole–dipole interactions. Consequently, these data suggest that propionic acid is more polar than isopropanol.

## Contributors

- Anonymous

Video at 11.3.2a by Christopher Rozitis @ YouTube

Video at 11.3.2b by Cambridge University @ YouTube

Video at 11.3.3 by Fink Feed Systems @ YouTube

Video at 11.3.4 by Safeguard Europe @ YouTube

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# 11.4: Vapor Pressure

**Learning Objectives**

- To know how and why the vapor pressure of a liquid varies with temperature.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressureThe pressure created over a liquid by the molecules of a liquid substance that have enough kinetic energy to escape to the vapor phase. of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

## Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 11.4.1), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy ($E_0$) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than $E_0$. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than $E_0$ has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization)The physical process by which atoms or molecules in the liquid phase enter the gas or vapor phase., where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

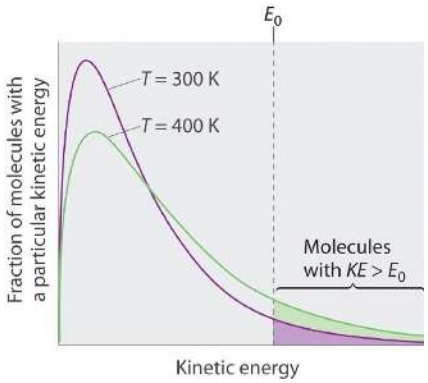



Figure 11.4.1 The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than $E_0$ can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 11.4.2 . When a liquid is introduced into an evacuated chamber (part (a) in Figure 11.4.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

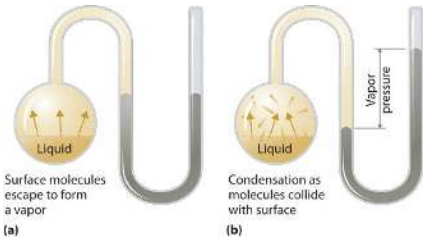



Figure 11.4.2 Vapor Pressure (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensationThe physical process by which atoms or molecules in the vapor phase enter the liquid phase. (part (b) in Figure 11.4.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 11.4.3 .

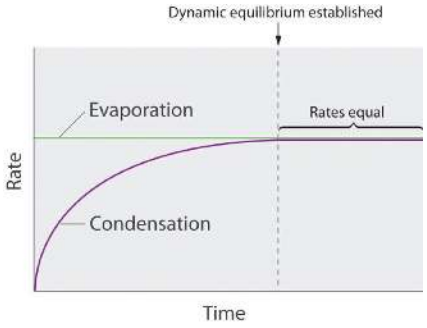



Figure 11.4.3 The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.

## Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibriumA state in which two opposing processes occur at the same rate, thus producing no net change in the system.. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressureThe pressure exerted by a vapor in dynamic equilibrium with its liquid. of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquidsA liquid with a relatively high vapor pressure. have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquidsA liquid with a relatively low vapor pressure. have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Table 11.3.1) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point (Table 11.3.1). It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 10.4.4 . Molecules that can hydrogen bond, such as

ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

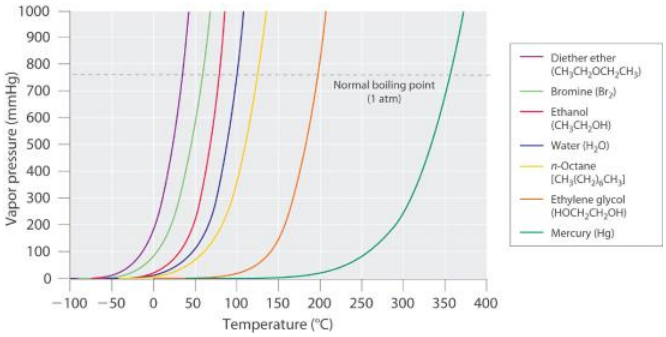



Figure 11.4.4 The Vapor Pressures of Several Liquids as a Function of Temperature The point at which the vapor pressure curve crosses the $P$ = 1 atm line (dashed) is the normal boiling point of the liquid.

## Note the Pattern

Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.

The exponential rise in vapor pressure with increasing temperature in Figure 11.4.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.For a review of natural logarithms, refer to Essential Skills 6 in Section 11.9 .

$$ln\,(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{11.4.1}$$

where ln $P$ is the natural logarithm of the vapor pressure, $\Delta H_{vap}$ is the **enthalpy of vaporization**, $R$ is the universal gas constant [8.314 J/(mol·K)], $T$ is the temperature in Kelvin, and $C$ is the $y$-intercept, which is a constant for any given liquid. A plot of ln $P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 11.4.1, called the Clausius–Clapeyron equationA linear relationship that expresses the nonlinear relationship between the vapor pressure of a liquid and temperature: P is the pressure, $\Delta H_{vap}$, R is the gas constant, T is the absolute temperature, and C is a constant. The Clausius–Clapeyron equation can be used to calculate the heat of vaporization of a liquid from its measured vapor pressure at two or more temperatures., can be used to calculate the $\Delta H_{vap}$ of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine $\Delta H_{vap}$ is to measure the vapor pressure of a liquid at two temperatures and insert the values of $P$ and $T$ for these points into Equation 11.4.2, which is derived from the Clausius–Clapeyron equation:

$$ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11.4.2}$$

Conversely, if we know $\Delta H_{vap}$ and the vapor pressure $P_1$ at any temperature $T_1$, we can use Equation 10.4.2 to calculate the vapor pressure $P_2$ at any other temperature $T_2$, as shown in Example 6.

## Example 11.4.1

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

| $T$ (°C) | 80.0 | 100 | 120 | 140 |
|---|---|---|---|---|
| $P$ (torr) | 0.0888 | 0.2729 | 0.7457 | 1.845 |

From these data, calculate the enthalpy of vaporization ($\Delta H_{vap}$) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

**Given:** vapor pressures at four temperatures

**Asked for:** $\Delta H_{vap}$ of mercury and vapor pressure at 160°C

**Strategy:**

A. Use Equation 11.4.2 to obtain $\Delta H_{vap}$ directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of $\Delta H_{vap}$ into Equation 11.4.2 to obtain the unknown pressure ($P_2$).

**Solution:**

**A** The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 11.4.1 and find the value of $\Delta H_{vap}$ from the slope of the line, an alternative approach is to use Equation 11.4.2 to obtain $\Delta H_{vap}$ directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvins because the equation requires absolute temperatures. Substituting the values measured at 80.0°C ($T_1$) and 120.0°C ($T_2$) into Equation 11.4.2 gives

$$ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right) \tag{11.4.1}$$

$$ln\,(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right) \tag{11.4.2}$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol \tag{11.4.3}$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol \tag{11.4.4}$$

**B** We can now use this value of $\Delta H_{vap}$ to calculate the vapor pressure of the liquid ($P_2$) at 160.0°C ($T_2$):

$$ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right) \tag{11.4.5}$$

Using the relationship $e^{\ln x} = x$, we have

$$ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86 \tag{11.4.6}$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5 \tag{11.4.7}$$

$$P_2 = 4.21 Torr \tag{11.4.8}$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

Exercise

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

**Answer:** 1896°C

## Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 11.4.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 11.4.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

### Note the Pattern

As pressure increases, the boiling point of a liquid increases and vice versa.

**Table 11.4.1 The Boiling Points of Water at Various Locations on Earth**

| Place | Altitude above Sea Level (ft) | Atmospheric Pressure (mmHg) | Boiling Point of Water (°C) |
|---|---|---|---|
| Mt. Everest, Nepal/Tibet | 29,028 | 240 | 70 |
| Bogota, Colombia | 11,490 | 495 | 88 |
| Denver, Colorado | 5280 | 633 | 95 |
| Washington, DC | 25 | 759 | 100 |
| Dead Sea, Israel/Jordan | −1312 | 799 | 101.4 |

### Example 11.4.2

Use Figure 11.4.4 to estimate the following.

1. the boiling point of water in a pressure cooker operating at 1000 mmHg
2. the pressure required for mercury to boil at 250°C

**Given:** data in Figure 11.4.4 , pressure, and boiling point

**Asked for:** corresponding boiling point and pressure

**Strategy:**

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 10.4.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

**Solution:**

1. **A** The vapor pressure curve of water intersects the $P$ = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
2. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

Exercise

Use the data in Figure 10.4.4 to estimate the following.

1. the normal boiling point of ethylene glycol
2. the pressure required for diethyl ether to boil at 20°C.

**Answer**

1. 200°C
2. 450 mmHg

## Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

## Key Takeaways

- The equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- The relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

## Key Equations

**Clausius–Clapeyron equation**

$$ln\,(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{11.4.1}$$

**Using vapor pressure at two temperatures to calculate $\Delta H_{vap}$**

$$ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11.4.2}$$

## Conceptual Problems

1. What is the relationship between the boiling point, vapor pressure, and temperature of a substance and atmospheric pressure?
2. What is the difference between a volatile liquid and a nonvolatile liquid? Suppose that two liquid substances have the same molecular mass, but one is volatile and the other is nonvolatile. What differences in the molecular structures of the two substances could account for the differences in volatility?
3. An “old wives’ tale” states that applying ethanol to the wrists of a child with a very high fever will help to reduce the fever because blood vessels in the wrists are close to the skin. Is there a scientific basis for this recommendation? Would water be as effective as ethanol?
4. Why is the air over a strip of grass significantly cooler than the air over a sandy beach only a few feet away?
5. If gasoline is allowed to sit in an open container, it often feels much colder than the surrounding air. Explain this observation. Describe the flow of heat into or out of the system, as well as any transfer of mass that occurs. Would the temperature of a sealed can of gasoline be higher, lower, or the same as that of the open can? Explain your answer.
6. What is the relationship between the vapor pressure of a liquid and
    1. its temperature?
    2. the surface area of the liquid?
    3. the pressure of other gases on the liquid?
    4. its viscosity?
7. At 25°C, benzene has a vapor pressure of 12.5 kPa, whereas the vapor pressure of acetic acid is 2.1 kPa. Which is more volatile? Based on the intermolecular interactions in the two liquids, explain why acetic acid has the lower vapor pressure.

## Numerical Problems

1. Acetylene ($C_2H_2$), which is used for industrial welding, is transported in pressurized cylinders. Its vapor pressure at various temperatures is given in the following table. Plot the data and use your graph to estimate the vapor pressure of acetylene at 293 K. Then use your graph to determine the value of $\Delta H_{vap}$ for acetylene. How much energy is required to vaporize 2.00 g of acetylene at 250 K?

| ***T* (K)** | 145 | 155 | 175 | 200 | 225 | 250 | 300 |
|---|---|---|---|---|---|---|---|
| ***P* (mmHg)** | 1.3 | 7.8 | 32.2 | 190 | 579 | 1370 | 5093 |

2. The following table gives the vapor pressure of water at various temperatures. Plot the data and use your graph to estimate the vapor pressure of water at 25°C and at 75°C. What is the vapor pressure of water at 110°C? Use these data to determine the value of $\Delta H_{vap}$ for water.

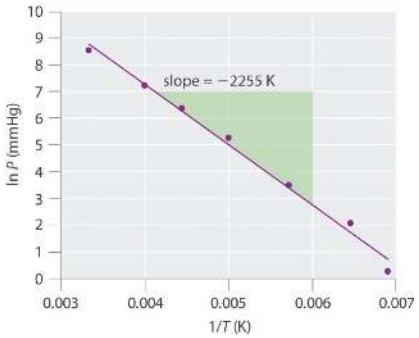
| ***T* (°C)** | 0 | 10 | 30 | 50 | 60 | 80 | 100 |
|---|---|---|---|---|---|---|---|
| ***P* (mmHg)** | 4.6 | 9.2 | 31.8 | 92.6 | 150 | 355 | 760 |

3. The $\Delta H_{vap}$ of carbon tetrachloride is 29.8 kJ/mol, and its normal boiling point is 76.8°C. What is its boiling point at 0.100 atm?
4. The normal boiling point of sodium is 883°C. If $\Delta H_{vap}$ is 97.4 kJ/mol, what is the vapor pressure (in millimeters of mercury) of liquid sodium at 300°C?
5. An unknown liquid has a vapor pressure of 0.860 atm at 63.7°C and a vapor pressure of 0.330 atm at 35.1°C. Use the data in Table 11.5.1 to identify the liquid.
6. An unknown liquid has a boiling point of 75.8°C at 0.910 atm and a boiling point of 57.2°C at 0.430 atm. Use the data in Table 11.5.1 to identify the liquid.
7. If the vapor pressure of a liquid is 0.850 atm at 20°C and 0.897 atm at 25°C, what is the normal boiling point of the liquid?
8. If the vapor pressure of a liquid is 0.799 atm at 99.0°C and 0.842 atm at 111°C, what is the normal boiling point of the liquid?
9. The vapor pressure of liquid $SO_2$ is 33.4 torr at −63.4°C and 100.0 torr at −47.7 K.
    1. What is the $\Delta H_{vap}$ of $SO_2$?
    2. What is its vapor pressure at −24.5 K?
    3. At what temperature is the vapor pressure equal to 220 torr?
10. The vapor pressure of $CO_2$ at various temperatures is given in the following table:

| ***T* (°C)** | −120 | −110 | −100 | −90 |
|---|---|---|---|---|
| ***P* (torr)** | 9.81 | 34.63 | 104.81 | 279.5 |

    1. What is $\Delta H_{vap}$ over this temperature range?
    2. What is the vapor pressure of $CO_2$ at −70°C?
    3. At what temperature does $CO_2$ have a vapor pressure of 310 torr?

## Answers

1. 


   vapor pressure at 273 K is 3050 mmHg; $\Delta H_{vap}$ = 18.7 kJ/mol, 1.44 kJ

2. 
3. 12.5°C
4. 
5. $\Delta H_{vap}$ = 28.9 kJ/mol, *n*-hexane
6. 
7. $\Delta H_{vap}$ = 7.81 kJ/mol, 36°C
8. 
9. 
10. 

## Contributors

- Anonymous

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# 11.5: Changes of State

**Learning Objectives**

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid $CO_2$, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changesA change of state that occurs when any of the three forms of matter (solids, liquids, and gases) is converted to either of the other two.. The six most common phase changes are shown in Figure 11.5.1.

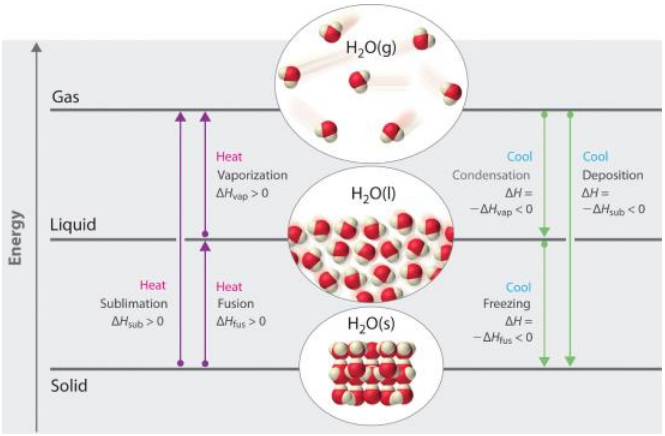



Figure 11.5.1 The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed Enthalpy changes that accompany phase transitions are indicated by purple and green arrows.

## Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 11.5.1.

In Chapter 9, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion ($\Delta H_{fus}$)**, the energy required to convert from a solid to a liquid, a process known as fusion (or melting)The conversion of a solid to a liquid., as well as the normal boiling points and enthalpies of vaporization ($\Delta H_{vap}$) of selected compounds are listed in Table 10.5.1. The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

**Table 11.5.1 Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances**

| Substance | Melting Point (°C) | $\Delta H_{fus}$ (kJ/mol) | Boiling Point (°C) | $\Delta H_{vap}$ (kJ/mol) |
|---|---|---|---|---|
| $N_2$ | −210.0 | 0.71 | −195.8 | 5.6 |
| HCl | −114.2 | 2.00 | −85.1 | 16.2 |
| $Br_2$ | −7.2 | 10.6 | 58.8 | 30.0 |
| $CCl_4$ | −22.6 | 2.56 | 76.8 | 29.8 |
| $CH_3CH_2OH$ (ethanol) | −114.1 | 4.93 | 78.3 | 38.6 |
| $CH_3(CH_2)_4CH_3$ (*n*-hexane) | −95.4 | 13.1 | 68.7 | 28.9 |
| $H_2O$ | 0 | 6.01 | 100 | 40.7 |
| Na | 97.8 | 2.6 | 883 | 97.4 |
| NaF | 996 | 33.4 | 1704 | 176.1 |

### Note the Pattern

$\Delta H$ is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimationThe conversion of a solid directly to a gas (without an intervening liquid phase).. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation ($\Delta H_{sub}$)The enthalpy change that accompanies the conversion of a solid directly to a gas.. Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include $CO_2$ (dry ice); iodine (Figure 11.5.2 ); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 11.5.1 the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*; this is an application of Hess's law. (For more information about Hess's law, see Section 9.2 ).

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{11.5.1}$$

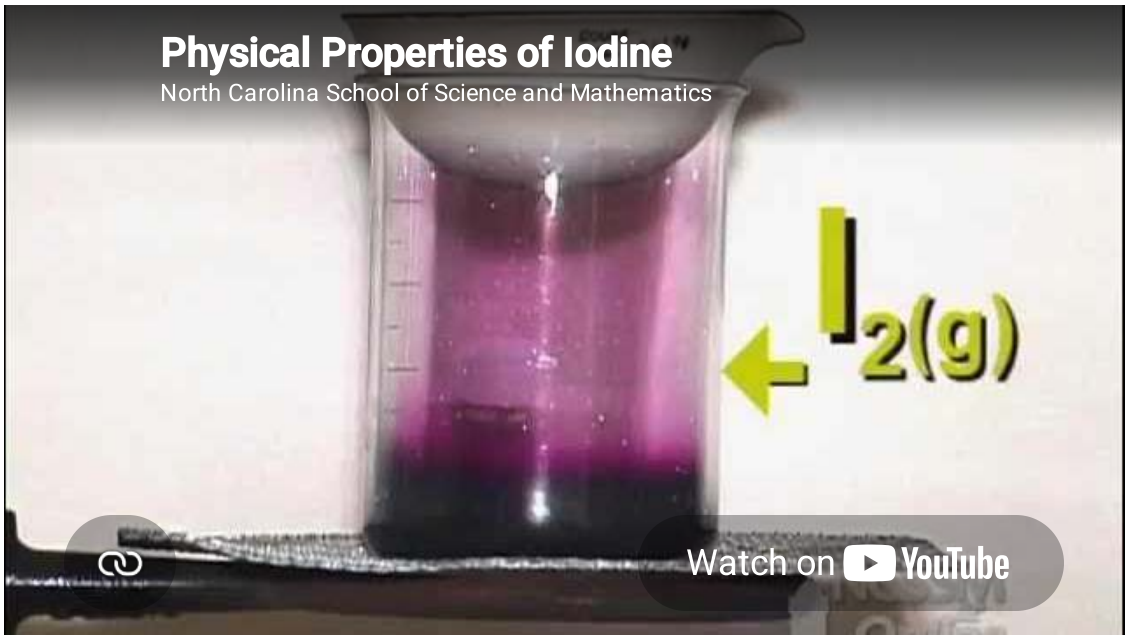





**Figure 11.5.2 The Sublimation of Solid Iodine** When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the $I_2$ vapor comes in contact with a cold surface, it deposits $I_2$ crystals.

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs) discussed in Section7.6 in connection with the ozone layer. The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C, as demonstrated later in Example 8.

## Temperature Curves

The processes on the right side of Figure 11.5.1 —freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

## Heating Curves

Figure 11.5.3 shows a heating curveA plot of the temperature of a substance versus the heat added or versus the heating time at a constant rate of heating., a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat ($C_s$)The number of joules required to raise the temperature of 1 g of a substance by 1°C. of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

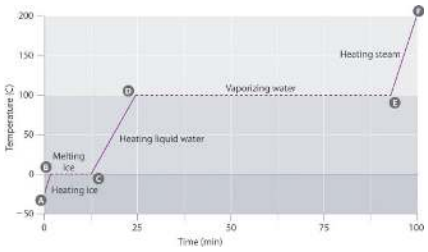



Figure 11.5.3 A Heating Curve for Water This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

### Note the Pattern

The temperature of a sample does not change during a phase change.

If heat is added at a constant rate, as in Figure 11.5.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 11.5.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquidAn unstable liquid at a temperature and pressure at which it should be a gas. is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

## Cooling Curves

The cooling curveA plot of the temperature of a substance versus the heat removed or versus the cooling time at a constant rate of cooling., a plot of temperature versus cooling time, in Figure 11.5.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 11.5.3 , the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquidA metastable liquid phase that exists below the normal melting point of a substance.. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystalA solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization.), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

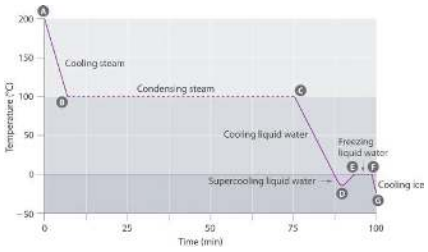



Figure 11.5.4 A Cooling Curve for Water This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid $CO_2$ (dry ice) into the cloud from an airplane. Solid $CO_2$ sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the $CO_2$ sublimes, it absorbs heat from the cloud, often with the desired results.

### Example 11.5.1

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g·°C) and 2.062 J/(g·°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

**Given:** mass, volume, initial temperature, density, specific heats, and $\Delta H_{fus}$

**Asked for:** final temperature

**Strategy:**

Substitute the values given into the general equation relating heat gained to heat lost (Equation 9.6.7) to obtain the final temperature of the mixture.

**Solution:**

Recall from Chapter 9 that when two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where $q$ is heat, $m$ is mass, $C_s$ is the specific heat, and $\Delta T$ is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0C:

$$q_{lost} = -q_{gained}$$

$$m_{iced\ tea}C_s\left(H_2O\right)\Delta T_{iced\ tea} = -\left[m_{ice}C_s\left(H_2O\right)\Delta T_{ice}\right] + mol_{ice}\Delta H_{fus}\left(H_2O\right)$$

$$500\ \cancel{g}\left[4.184\ J/\left(\cancel{g}\cdot{}^{o}C\right)\right]\left(T_f - 20.0\ {}^{o}C\right)$$
$$= -50\ \cancel{g}\left[4.184\ J/\left(\cancel{g}\cdot{}^{o}C\right)\right]\left(T_f - 0.0\ {}^{o}C\right) - \frac{50.0\ \cancel{g}}{18.0\ \cancel{g}/\cancel{mol}}6.01\times10^{3}\ J/\cancel{mol}$$

$$(2090\ J/^oC)\,(T_f - 20.0\ ^oC) = -\,(209\ J/^oC)\,T_f - 1.67 \times 10^4 J$$

$$2.53 \times 10^4 J = (2310\ J/^oC)\,T_f$$

$$11.0\ ^oC = T_f$$

Exercise

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you can't remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 8

**Answer:** 200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

## Summary

Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion ($\Delta H_{\text{fus}}$). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization ($\Delta H_{\text{vap}}$). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation ($\Delta H_{\text{sub}}$)** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

## Key Takeaway

- Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes.

## Conceptual Problems

1. In extremely cold climates, snow can disappear with no evidence of its melting. How can this happen? What change(s) in state are taking place? Would you expect this phenomenon to be more common at high or low altitudes? Explain your answer.
2. Why do car manufacturers recommend that an automobile should not be left standing in subzero temperatures if its radiator contains only water? Car manufacturers also warn car owners that they should check the fluid level in a radiator only when the engine is cool. What is the basis for this warning? What is likely to happen if it is ignored?
3. Use Hess's law and a thermochemical cycle to show that, for any solid, the enthalpy of sublimation is equal to the sum of the enthalpy of fusion of the solid and the enthalpy of vaporization of the resulting liquid.
4. Three distinct processes occur when an ice cube at −10°C is used to cool a glass of water at 20°C. What are they? Which causes the greatest temperature change in the water?
5. When frost forms on a piece of glass, crystals of ice are deposited from water vapor in the air. How is this process related to sublimation? Describe the energy changes that take place as the water vapor is converted to frost.
6. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?
    1. ice melting
    2. distillation

3. condensation forming on a window
4. the use of dry ice to create a cloud for a theatrical production

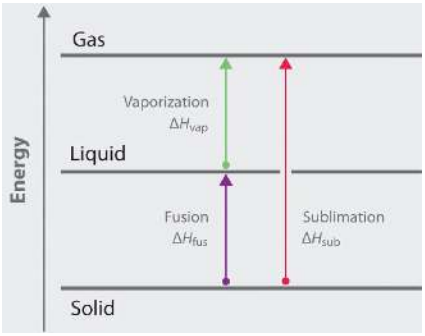
7. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?
    1. evaporation of methanol
    2. crystallization
    3. liquefaction of natural gas
    4. the use of naphthalene crystals to repel moths
8. Why do substances with high enthalpies of fusion tend to have high melting points?
9. Why is the enthalpy of vaporization of a compound invariably much larger than its enthalpy of fusion?
10. What is the opposite of fusion, sublimation, and condensation? Describe the phase change in each pair of opposing processes and state whether each phase change is exothermic or endothermic.
11. Draw a typical heating curve (temperature versus amount of heat added at a constant rate) for conversion of a solid to a liquid and then to a gas. What causes some regions of the plot to have a positive slope? What is happening in the regions of the plot where the curve is horizontal, meaning that the temperature does not change even though heat is being added?
12. If you know the mass of a sample of a substance, how could you use a heating curve to calculate the specific heat of the substance, as well as the change in enthalpy associated with a phase change?
13. Draw the heating curve for a liquid that has been superheated. How does this differ from a normal heating curve for a liquid? Draw the cooling curve for a liquid that has been supercooled. How does this differ from a normal cooling curve for a liquid?

## Answers

1. When snow disappears without melting, it must be subliming directly from the solid state to the vapor state. The rate at which this will occur depends solely on the partial pressure of water, not on the total pressure due to other gases. Consequently, altitude (and changes in atmospheric pressure) will not affect the rate of sublimation directly.
2. 
3. The general equations and enthalpy changes for the changes of state involved in converting a solid to a gas are:

$$\begin{array}{ll} solid \rightarrow liquid & \Delta H_{fus} \\ liquid \rightarrow gas & \Delta H_{vap} \\ solid \rightarrow gas & \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \end{array}$$

   The relationship between these enthalpy changes is shown schematically in the thermochemical cycle below:



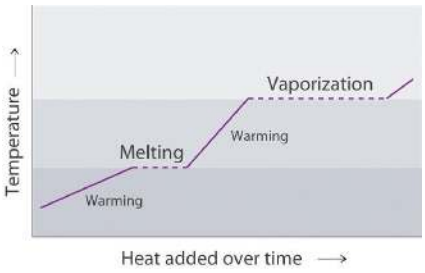

4. 
5. The formation of frost on a surface is an example of deposition, which is the reverse of sublimation. The change in enthalpy for deposition is equal in magnitude, but opposite in sign, to $\Delta H_{sub}$, which is a positive number: $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$.
6. 
7. 1. liquid + heat → vapor: endothermic
    2. liquid → solid + heat: exothermic

3. gas → liquid + heat: exothermic
4. solid + heat → vapor: endothermic

8.

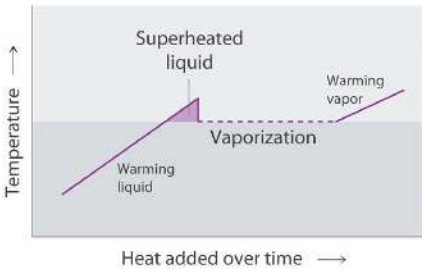
9. The enthalpy of vaporization is larger than the enthalpy of fusion because vaporization requires the addition of enough energy to disrupt all intermolecular interactions and create a gas in which the molecules move essentially independently. In contrast, fusion requires much less energy, because the intermolecular interactions in a liquid and a solid are similar in magnitude in all condensed phases. Fusion requires only enough energy to overcome the intermolecular interactions that lock molecules in place in a lattice, thereby allowing them to move more freely.

10.

11. 

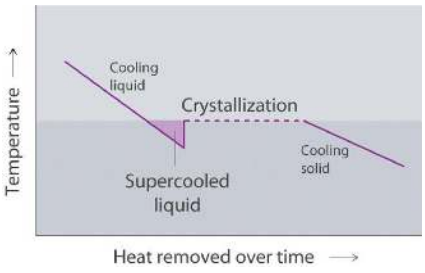

The portions of the curve with a positive slope correspond to heating a single phase, while the horizontal portions of the curve correspond to phase changes. During a phase change, the temperature of the system does not change, because the added heat is melting the solid at its melting point or evaporating the liquid at its boiling point.

12.

13. 


A superheated liquid exists temporarily as liquid with a temperature above the normal boiling point of the liquid. When a supercooled liquid boils, the temperature drops as the liquid is converted to vapor.

Conversely, a supercooled liquid exists temporarily as a liquid with a temperature lower than the normal melting point of the solid. As shown below, when a supercooled liquid crystallizes, the temperature increases as the liquid is converted to a solid.




## Numerical Problems

1. The density of oxygen at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of oxygen.

| *T* **(K)** | 60 | 70 | 80 | 90 | 100 | 120 | 140 |
|---|---|---|---|---|---|---|---|
| *d* **(mol/L)** | 40.1 | 38.6 | 37.2 | 35.6 | 0.123 | 0.102 | 0.087 |

2. The density of propane at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of propane.

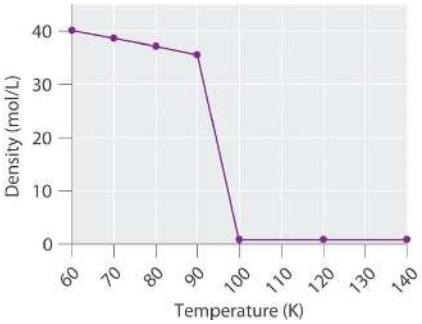
| *T* (K) | 100 | 125 | 150 | 175 | 200 | 225 | 250 | 275 |
|---|---|---|---|---|---|---|---|---|
| *d* (mol/L) | 16.3 | 15.7 | 15.0 | 14.4 | 13.8 | 13.2 | 0.049 | 0.044 |

3. Draw the cooling curve for a sample of the vapor of a compound that has a melting point of 34°C and a boiling point of 77°C as it is cooled from 100°C to 0°C.
4. Propionic acid has a melting point of −20.8°C and a boiling point of 141°C. Draw a heating curve showing the temperature versus time as heat is added at a constant rate to show the behavior of a sample of propionic acid as it is heated from −50°C to its boiling point. What happens above 141°C?
5. A 0.542 g sample of $I_2$ requires 96.1 J of energy to be converted to vapor. What is the enthalpy of sublimation of $I_2$?
6. A 2.0 L sample of gas at 210°C and 0.762 atm condenses to give 1.20 mL of liquid, and 476 J of heat is released during the process. What is the enthalpy of vaporization of the compound?
7. One fuel used for jet engines and rockets is aluminum borohydride [$Al(BH_4)_3$], a liquid that readily reacts with water to produce hydrogen. The liquid has a boiling point of 44.5°C. How much energy is needed to vaporize 1.0 kg of aluminum borohydride at 20°C, given a $\Delta H_{vap}$ of 30 kJ/mol and a molar heat capacity ($C_p$) of 194.6 J/(mol·K)?
8. How much energy is released when freezing 100.0 g of dimethyl disulfide ($C_2H_6S_2$) initially at 20°C? Use the following information: melting point = −84.7°C, $\Delta H_{fus}$ = 9.19 kJ/mol, $C_p$ = 118.1 J/(mol·K).

*The following four problems use the following information (the subscript p indicates measurements taken at constant pressure): $\Delta H_{fus}(H_2O)$ = 6.01 kJ/mol, $\Delta H_{vap}(H_2O)$ = 40.66 kJ/mol, $C_{p(s)}$(crystalline $H_2O$) = 38.02 J/(mol·K), $C_{p(l)}$(liquid $H_2O$) = 75.35 J/(mol·K), and $C_{p(g)}$($H_2O$ gas) = 33.60 J/(mol·K).*

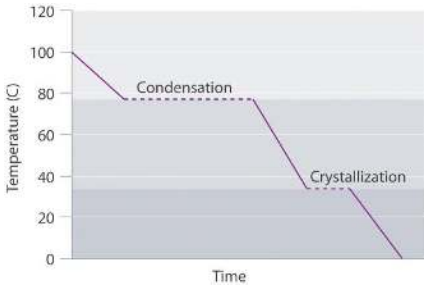
9. How much heat is released in the conversion of 1.00 L of steam at 21.9 atm and 200°C to ice at −6.0°C and 1 atm?
10. How much heat must be applied to convert a 1.00 g piece of ice at −10°C to steam at 120°C?
11. How many grams of boiling water must be added to a glass with 25.0 g of ice at −3°C to obtain a liquid with a temperature of 45°C?
12. How many grams of ice at −5.0°C must be added to 150.0 g of water at 22°C to give a final temperature of 15°C?

## Answers

1. 


   The transition from a liquid to a gaseous phase is accompanied by a drastic decrease in density. According to the data in the table and the plot, the boiling point of liquid oxygen is between 90 and 100 K (actually 90.2 K).

2.

3. 

4.
5. 45.0 kJ/mol
6.
7. 488 kJ
8.
9. 32.6 kJ
10.
11. 57 g
12.

## Contributors

- Anonymous

Video 11.5.3 from the **North Carolina School of Science and Mathematics** @ YouTube

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# 11.6: Critical Temperature and Pressure

**Learning Objectives**

- To know what is meant by the critical temperature and pressure of a liquid.

In Section 11.1, we saw that a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature ($T_c$), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure ($P_c$), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Table 11.6.1.

### Note the Pattern

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

**Table 11.6.1 Critical Temperatures and Pressures of Some Simple Substances**

| Substance | $T_c$ (°C) | $P_c$ (atm) |
|---|---|---|
| $NH_3$ | 132.4 | 113.5 |
| $CO_2$ | 31.0 | 73.8 |
| $CH_3CH_2OH$ (ethanol) | 240.9 | 61.4 |
| He | −267.96 | 2.27 |
| Hg | 1477 | 1587 |
| $CH_4$ | −82.6 | 46.0 |
| $N_2$ | −146.9 | 33.9 |
| $H_2O$ | 374.0 | 217.7 |

## Supercritical Fluids

To understand what happens at the critical point, consider the effects of temperature and pressure on the densities of liquids and gases, respectively. As the temperature of a liquid increases, its density decreases. As the pressure of a gas increases, its density increases. At the critical point, the liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluidThe single, dense fluid phase that exists above the critical temperature of a substance., which exhibits many of the properties of a gas but has a density more typical of a liquid. For example, the density of water at its critical point ($T$ = 374°C, $P$ = 217.7 atm) is 0.32 g/mL, about one-third that of liquid water at room temperature but much greater than that of water vapor under most conditions. The transition between a liquid/gas mixture and a supercritical phase is demonstrated for a sample of chlorine in Figure 11.6.1 . At the critical temperature, the meniscus separating the liquid and gas phases disappears.

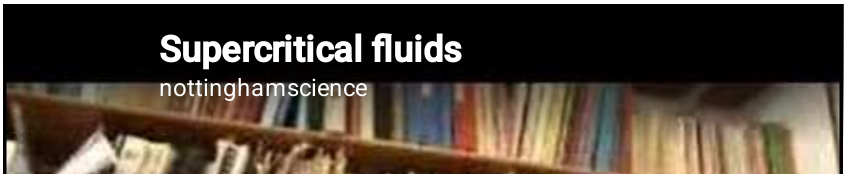





**Figure 11.6.1 Supercritical fluids** Professor Martyn Poliakoff demonstrates supercritical fluids. Below the critical temperature the meniscus between the liquid and gas phases is apparent. At the critical temperature, the meniscus disappears because the density of the vapor is equal to the density of the liquid. Above $T_c$, a dense homogeneous fluid fills the tube.

In the last few years, supercritical fluids have evolved from laboratory curiosities to substances with important commercial applications. For example, carbon dioxide has a low critical temperature (31°C), a comparatively low critical pressure (73 atm), and low toxicity, making it easy to contain and relatively safe to manipulate. Because many substances are quite soluble in supercritical $CO_2$, commercial processes that use it as a solvent are now well established in the oil industry, the food industry, and others. Supercritical $CO_2$ is pumped into oil wells that are no longer producing much oil to dissolve the residual oil in the underground reservoirs. The less-viscous solution is then pumped to the surface, where the oil can be recovered by evaporation (and recycling) of the $CO_2$. In the food, flavor, and fragrance industry, supercritical $CO_2$ is used to extract components from natural substances for use in perfumes, remove objectionable organic acids from hops prior to making beer, and selectively extract caffeine from whole coffee beans without removing important flavor components. The latter process was patented in 1974, and now virtually all decaffeinated coffee is produced this way. The earlier method used volatile organic solvents such as methylene chloride (dichloromethane [$CH_2Cl_2$], boiling point = 40°C), which is difficult to remove completely from the beans and is known to cause cancer in laboratory animals at high doses.

### Example 11.6.1

Arrange methanol, *n*-butane, *n*-pentane, and $N_2O$ in order of increasing critical temperatures.

**Given:** compounds

**Asked for:** order of increasing critical temperatures

**Strategy:**

**A** Identify the intermolecular forces in each molecule and then assess the strengths of those forces.

**B** Arrange the compounds in order of increasing critical temperatures.

**Solution:**

**A** The critical temperature depends on the strength of the intermolecular interactions that hold a substance together as a liquid. In $N_2O$, a slightly polar substance, weak dipole–dipole interactions and London dispersion forces are important. Butane ($C_4H_{10}$) and pentane ($C_5H_{12}$) are larger, nonpolar molecules that exhibit only London dispersion forces. Methanol, in contrast, should have substantial intermolecular hydrogen bonding interactions. Because hydrogen bonds are stronger than the other intermolecular forces, methanol will have the highest $T_c$. London forces are more important for pentane than for butane because of its larger size, so *n*-pentane will have a higher $T_c$ than *n*-butane. The only remaining question is whether $N_2O$ is polar enough to have stronger intermolecular interactions than pentane or butane. Because the electronegativities of O and N are quite similar, the answer is probably no, so $N_2O$ should have the lowest $T_c$. **B** We therefore predict the order of increasing critical temperatures as $N_2O$ < *n*-butane < *n*-pentane < methanol. The actual values are $N_2O$ (36.9°C) < *n*-butane (152.0°C) < *n*-pentane (196.9°C) < methanol (239.9°C). This is the same order as their normal boiling points—$N_2O$ (−88.7°C) < *n*-butane (−0.2°C) < *n*-pentane (36.0°C) <

methanol (65°C)—because both critical temperature and boiling point depend on the relative strengths of the intermolecular interactions.

Exercise

Arrange ethanol, methanethiol ($CH_3SH$), ethane, and *n*-hexanol in order of increasing critical temperatures.

**Answer:** ethane (32.3°C) < methanethiol (196.9°C) < ethanol (240.9°C) < *n*-hexanol (336.9°C)

## Molten Salts and Ionic Liquids

Heating a salt to its melting point produces a molten saltA salt that has been heated to its melting point.. If we heated a sample of solid NaCl to its melting point of 801°C, for example, it would melt to give a stable liquid that conducts electricity. The characteristics of molten salts other than electrical conductivity are their high heat capacity, ability to attain very high temperatures (over 700°C) as a liquid, and utility as solvents because of their relatively low toxicity.

Molten salts have many uses in industry and the laboratory. For example, in solar power towers in the desert of California, mirrors collect and focus sunlight to melt a mixture of sodium nitrite and sodium nitrate. The heat stored in the molten salt is used to produce steam that drives a steam turbine and a generator, thereby producing electricity from the sun for southern California.

Due to their low toxicity and high thermal efficiency, molten salts have also been used in nuclear reactors to enable operation at temperatures greater than 750°C. One prototype reactor tested in the 1950s used a fuel and a coolant consisting of molten fluoride salts, including NaF, $ZrF_4$, and $UF_4$. Molten salts are also useful in catalytic processes such as coal gasification, in which carbon and water react at high temperatures to form CO and $H_2$.

### Note the Pattern

Molten salts are good electrical conductors, have a high heat capacity, can maintain a high temperature as a liquid, and are relatively nontoxic.

Although molten salts have proven highly useful, more recently chemists have been studying the characteristics of ionic liquidsIonic substances that are liquids at room temperature and pressure and that consist of small, symmetrical anions combined with larger, symmetrical organic cations that prevent the formation of a highly organized structure., ionic substances that are *liquid* at room temperature and pressure. These substances consist of small, symmetrical anions, such as $PF_6^-$ and $BF_4^-$, combined with larger, asymmetrical organic cations that prevent the formation of a highly organized structure, resulting in a low melting point. By varying the cation and the anion, chemists can tailor the liquid to specific needs, such as using a solvent in a given reaction or extracting specific molecules from a solution. For example, an ionic liquid consisting of a bulky cation and anions that bind metal contaminants such as mercury and cadmium ions can remove those toxic metals from the environment. A similar approach has been applied to removing uranium and americium from water contaminated by nuclear waste.

### Note the Pattern

Ionic liquids consist of small, symmetrical anions combined with larger asymmetrical cations, which produce a highly polar substance that is a liquid at room temperature and pressure.

The initial interest in ionic liquids centered on their use as a low-temperature alternative to molten salts in batteries for missiles, nuclear warheads, and space probes. Further research revealed that ionic liquids had other useful properties—for example, some could dissolve the black rubber of discarded tires, allowing it to be recovered for recycling. Others could be used to produce commercially important organic compounds with high molecular mass, such as Styrofoam and Plexiglas, at rates 10 times faster than traditional methods.

### Summary

A substance cannot form a liquid above its **critical temperature**, regardless of the applied pressure. Above the critical temperature, the molecules have enough kinetic energy to overcome the intermolecular attractive forces. The minimum pressure needed to liquefy a substance at its critical temperature is its **critical pressure**. The combination of the critical temperature and critical pressure of a substance is its **critical point**. Above the critical temperature and pressure, a substance exists as a dense fluid called a **supercritical fluid**, which resembles a gas in that it completely fills its container but has a density comparable to that of a liquid. A

**molten salt** is a salt heated to its melting point, giving a stable liquid that conducts electricity. **Ionic liquids** are ionic substances that are liquids at room temperature. Their disorganized structure results in a low melting point.

## Key Takeaway

- The critical temperature and critical pressure of a substance define its critical point, beyond which the substance forms a supercritical fluid.

## Conceptual Problems

1. Describe the changes that take place when a liquid is heated above its critical temperature. How does this affect the physical properties?
2. What is meant by the term *critical pressure*? What is the effect of increasing the pressure on a gas to above its critical pressure? Would it make any difference if the temperature of the gas was greater than its critical temperature?
3. Do you expect the physical properties of a supercritical fluid to be more like those of the gas or the liquid phase? Explain. Can an ideal gas form a supercritical fluid? Why or why not?
4. What are the limitations in using supercritical fluids to extract organic materials? What are the advantages?
5. Describe the differences between a molten salt and an ionic liquid. Under what circumstances would an ionic liquid be preferred over a molten salt?

## Contributors

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Video at 11.6.3 from nottingham science @ YouTube

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# 11.7: Phase Diagrams

**Learning Objectives**

- To understand the general features of a phase diagram.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagramA graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system. is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 11.7.1 ). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 11.7.1 ) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

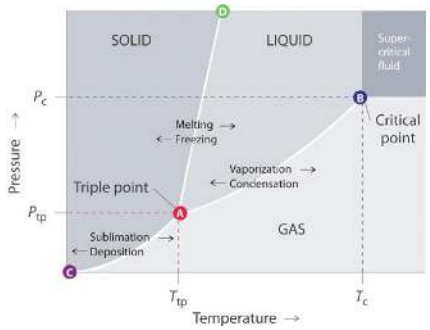



Figure 11.7.1 A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

### Note the Pattern

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

## General Features of a Phase Diagram

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 11.7.1 the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.4 . It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple pointThe point in a phase diagram where the solid/liquid, liquid/gas, and solid/gas lines intersect; it represents the only combination of temperature and pressure at which all three phases are in equilibrium and can therefore exist simultaneously.; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 11.7.1 , is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

## The Phase Diagram of Water

Figure 11.7.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric

pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

The phase diagram for water illustrated in part (b) in Figure 11.7.2 shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 11.7.1 ; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

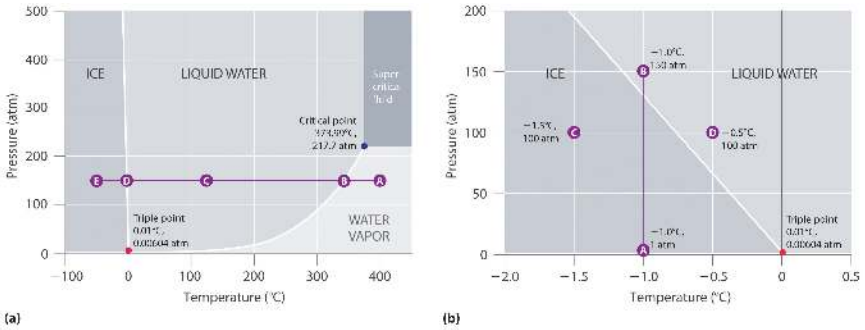



Figure 11.7.2 Two Versions of the Phase Diagram of Water (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 10.)

In part (b) in Figure 11.7.2 , point A is located at $P$ = 1 atm and $T$ = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

## The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of $CO_2$ (Figure 11.7.3 ) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid $CO_2$ cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid $CO_2$ sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid $CO_2$ is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed. Also notice the critical point at 30.98°C and 72.79 atm. In addition to the uses discussed in Section 11.6 , supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

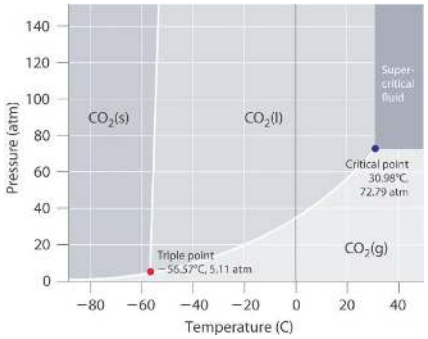



Figure 11.7.3 The Phase Diagram of Carbon Dioxide Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

## Example 11.7.1

Referring to the phase diagram of water in Figure 11.7.2 ,

1. predict the physical form of a sample of water at 400°C and 150 atm.
2. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

**Given:** phase diagram, temperature, and pressure

**Asked for:** physical form and physical changes

**Strategy:**

**A** Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.

**B** Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

**Solution:**

1. **A** Locate the starting point on the phase diagram in part (a) in Figure 11.7.2 . The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at $T$ = 400°C and $P$ = 150 atm is a gas.
2. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 11.7.2 . At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At $P$ = 150 atm and $T$ = −50°C, therefore, the sample is solid ice.

Exercise

Referring to the phase diagram of water in Figure 11.7.2 , predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

**Answer:** The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

## Summary

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a **phase diagram**, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point. Within a given region, only a single phase is stable, but along the lines that separate the regions, two phases are in equilibrium at a given temperature and pressure. The lines separating the three phases intersect at a single point, the **triple point**, which is the only combination of temperature and pressure at which all three phases can coexist in equilibrium. Water has an unusual phase diagram: its melting point decreases with increasing pressure

because ice is less dense than liquid water. The phase diagram of carbon dioxide shows that liquid carbon dioxide cannot exist at atmospheric pressure. Consequently, solid carbon dioxide sublimes directly to a gas.

### Key Takeaway

- A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system. It shows the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical region.

### Conceptual Problems

1. A phase diagram is a graphic representation of the stable phase of a substance at any combination of temperature and pressure. What do the lines separating different regions in a phase diagram indicate? What information does the slope of a line in a phase diagram convey about the physical properties of the phases it separates? Can a phase diagram have more than one point where three lines intersect?
2. If the slope of the line corresponding to the solid/liquid boundary in the phase diagram of water were positive rather than negative, what would be the effect on aquatic life during periods of subzero temperatures? Explain your answer.

### Answer

1. The lines in a phase diagram represent boundaries between different phases; at any combination of temperature and pressure that lies on a line, two phases are in equilibrium. It is physically impossible for more than three phases to coexist at any combination of temperature and pressure, but in principle there can be more than one triple point in a phase diagram. The slope of the line separating two phases depends upon their relative densities. For example, if the solid–liquid line slopes up and to the *right*, the liquid is less dense than the solid, while if it slopes up and to the *left*, the liquid is denser than the solid.
2.

### Numerical Problems

1. Naphthalene ($C_{10}H_8$) is the key ingredient in mothballs. It has normal melting and boiling points of 81°C and 218°C, respectively. The triple point of naphthalene is 80°C at 1000 Pa. Use these data to construct a phase diagram for naphthalene and label all the regions of your diagram.
2. Argon is an inert gas used in welding. It has normal boiling and freezing points of 87.3 K and 83.8 K, respectively. The triple point of argon is 83.8 K at 0.68 atm. Use these data to construct a phase diagram for argon and label all the regions of your diagram.

### Contributors

- Anonymous

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# 11.8: Liquid Crystals

**Learning Objectives**

- To describe the properties of liquid crystals.

When cooled, most liquids undergo a simple phase transitionAnother name for a phase change. to an ordered crystalline solid, a relatively rigid substance that has a fixed shape and volume. In the phase diagrams for these liquids, there are no regions between the liquid and solid phases. Thousands of substances are known, however, that exhibit one or more phases intermediate between the liquid state, in which the molecules are free to tumble and move past one another, and the solid state, in which the molecules or ions are rigidly locked into place. In these intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid. Hence they are called liquid crystalsA substance that exhibits phases that have properties intermediate between those of a crystalline solid and a normal liquid and possess long-range molecular order but still flow., and their unusual properties have found a wide range of commercial applications. They are used, for example, in the liquid crystal displays (LCDs) in digital watches, calculators, and computer and video displays.

The first documented example of a liquid crystal was reported by the Austrian Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholesteryl benzoate, and noticed that it behaved strangely as it melted. The white solid first formed a cloudy white liquid phase at 145°C, which reproducibly transformed into a clear liquid at 179°C. The transitions were completely reversible: cooling molten cholesteryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C.

In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as isotropicThe arrangement of molecules that is equally disordered in all directions., which means that it is equally disordered in all directions. Liquid crystals, in contrast, are anisotropicAn arrangement of molecules in which their properties depend on the direction they are measured.: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.

Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways, as shown in Figure 11.8.1. In the nematic phaseOne of three different ways that most liquid crystals can orient themselves. Only the long axes of the molecules are aligned, so they are free to rotate or to slide past one another., the molecules are not layered but are pointed in the same direction. As a result, the molecules are free to rotate or slide past one another. In the smectic phaseOne of three different ways that most liquid crystals can orient themselves. The long axes of the molecules are aligned (similar to the nematic phase), but the molecules are arranged in planes, too., the molecules maintain the general order of the nematic phase but are also aligned in layers. Several variants of the smectic phase are known, depending on the angle formed between the molecular axes and the planes of molecules. The simplest such structure is the so-called smectic A phase, in which the molecules can rotate about their long axes within a given plane, but they cannot readily slide past one another. In the cholesteric phaseOne of three different ways that most liquid crystals can orient themselves. The molecules are arranged in planes (similar to the smectic phase), but each layer is rotated by a certain amount with respect to those above and below it, giving it a helical structure., the molecules are directionally oriented and stacked in a helical pattern, with each layer rotated at a slight angle to the ones above and below it. As the degree of molecular ordering increases from the nematic phase to the cholesteric phase, the liquid becomes more opaque, although direct comparisons are somewhat difficult because most compounds form only one of these liquid crystal phases when the solid is melted or the liquid is cooled.

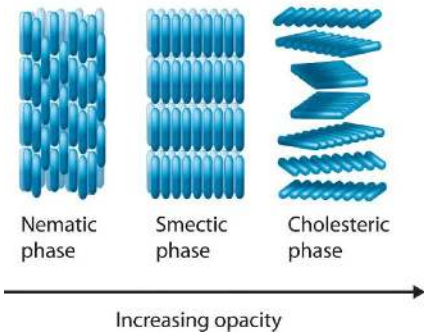



Figure 11.8.1 The Arrangement of Molecules in the Nematic, Smectic, and Cholesteric Liquid Crystal Phases In the *nematic* phase, only the long axes of the molecules are parallel, and the ends are staggered at random intervals. In the *smectic* phase, the long axes of the molecules are parallel, and the molecules are also arranged in planes. Finally, in the *cholesteric* phase, the molecules are arranged in layers; each layer is rotated with respect to the ones above and below it to give a spiral structure. The molecular order increases from the nematic phase to the smectic phase to the cholesteric phase, and the phases become increasingly opaque.

Molecules that form liquid crystals tend to be rigid molecules with polar groups that exhibit relatively strong dipole–dipole or dipole–induced dipole interactions, hydrogen bonds, or some combination of both. Some examples of substances that form liquid crystals are listed in Figure 11.8.2 along with their characteristic phase transition temperature ranges. In most cases, the intermolecular interactions are due to the presence of polar or polarizable groups. Aromatic rings and multiple bonds between carbon and nitrogen or oxygen are especially common. Moreover, many liquid crystals are composed of molecules with two similar halves connected by a unit having a multiple bond.

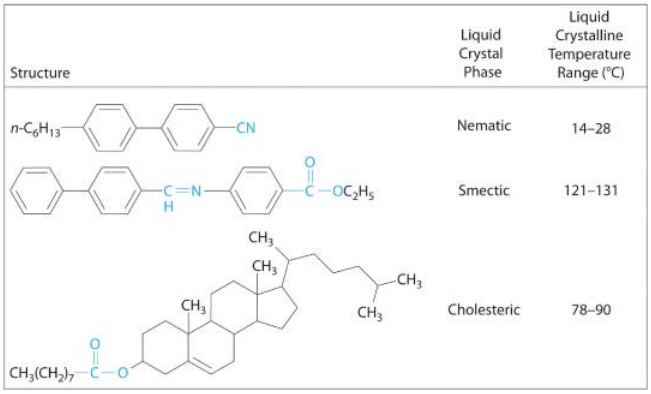



Figure 11.8.2 Structures of Typical Molecules That Form Liquid Crystals Polar or polarizable groups are indicated in blue.

Because of their anisotropic structures, liquid crystals exhibit unusual optical and electrical properties. The intermolecular forces are rather weak and can be perturbed by an applied electric field. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly. Nematic liquid crystals, for example, tend to be relatively translucent, but many of them become opaque when an electric field is applied and the molecular orientation changes. This behavior is ideal for producing dark images on a light or an opalescent background, and it is used in the LCDs in digital watches; handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation. Although each application differs in the details of its construction and operation, the basic principles are similar, as illustrated in Figure 11.8.3.

## Note the Pattern

Liquid crystals tend to form from long, rigid molecules with polar groups.

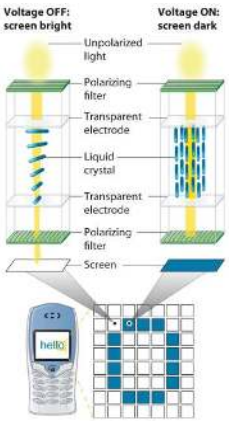



Figure 11.8.3 Schematic Drawing of an LCD Device, Showing the Various Layers Applying a voltage to selected segments of the device will produce any of the numbers. The device is a sandwich that contains several very thin layers, consisting of (from top to bottom) a sheet of polarizer to produce polarized light, a transparent electrode, a thin layer of a liquid crystalline substance, a second transparent electrode, a second polarizer, and a screen. Applying an electrical voltage to the liquid crystal changes its orientation slightly, which rotates the plane of the polarized light and makes the area appear dark.

Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light. Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures. It is therefore possible to build a liquid crystal thermometer that indicates temperature by color (Figure 11.8.4 ) and to use liquid crystals in heat-sensitive films to detect flaws in electronic board connections where overheating can occur.

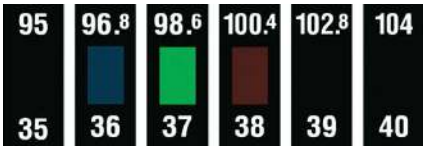



Figure 11.8.4 An Inexpensive Fever Thermometer That Uses Liquid Crystals Each section contains a liquid crystal sample with a different liquid crystalline range. The section whose liquid crystalline range corresponds to the temperature of the body becomes translucent (here shown in green), indicating the temperature.

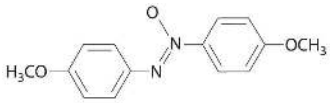
We also see the effect of liquid crystals in nature. Iridescent green beetles, known as jewel beetles, change color because of the light-reflecting properties of the cells that make up their external skeletons, not because of light absorption from their pigment. The cells form helices with a structure like those found in cholesteric liquid crystals. When the pitch of the helix is close to the wavelength of visible light, the cells reflect light with wavelengths that lead to brilliant metallic colors. Because a color change occurs depending on a person's angle of view, researchers in New Zealand are studying the beetles to develop a thin material that can be used as a currency security measure. The automobile industry is also interested in exploring such materials for use in paints that would change color at different viewing angles.

With only molecular structure as a guide, one cannot precisely predict which of the various liquid crystalline phases a given compound will actually form. One can, however, identify molecules containing the kinds of structural features that tend to result in liquid crystalline behavior, as demonstrated in Example 11.

## Example 11.8.1

Which molecule is most likely to form a liquid crystalline phase as the isotropic liquid is cooled?

1. isooctane (2,2,4-trimethylpentane)
2. ammonium thiocyanate [$NH_4(SCN)$]
3. *p*-azoxyanisole




*p*-Azoxyanisole

4. sodium decanoate {$Na[CH_3(CH_2)_8CO_2]$}

**Given:** compounds

**Asked for:** liquid crystalline behavior

**Strategy:**

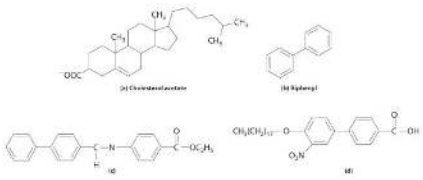
Determine which compounds have a rigid structure and contain polar groups. Those that do are likely to exhibit liquid crystal behavior.

**Solution:**

1. Isooctane is not long and rigid and contains no polar groups, so it is unlikely to exhibit liquid crystal behavior.
2. Ammonium thiocyanate is ionic, and ionic compounds tend to have high melting points, so it should not form a liquid crystalline phase. In fact, ionic compounds that form liquid crystals are very rare indeed.
3. *p*-Azoxyanisole combines two planar phenyl rings linked through a multiply bonded unit, and it contains polar groups. The combination of a long, rigid shape and polar groups makes it a reasonable candidate for a liquid crystal.
4. Sodium decanoate is the sodium salt of a straight-chain carboxylic acid. The *n*-alkyl chain is long, but it is flexible rather than rigid, so the compound is probably not a liquid crystal.

Exercise

Which compound is least likely to form a liquid crystal phase?



**Answer:** (b) Biphenyl; although it is rather long and rigid, it lacks any polar substituents.

## Summary

Many substances exhibit phases that have properties intermediate between those of a crystalline solid and a normal liquid. These substances, which possess long-range molecular order but still flow like liquids, are called **liquid crystals**. Liquid crystals are typically long, rigid molecules that can interact strongly with one another; they do not have **isotropic** structures, which are completely disordered, but rather have **anisotropic** structures, which exhibit different properties when viewed from different directions. In the **nematic phase**, only the long axes of the molecules are aligned, whereas in the **smectic phase**, the long axes of the molecules are parallel and the molecules are arranged in planes. In the **cholesteric phase**, the molecules are arranged in planes, but each layer is rotated by a certain amount with respect to those above and below it, giving a helical structure.

## Key Takeaway

- Liquid crystals tend to consist of rigid molecules with polar groups, and their anisotropic structures exhibit unusual optical and electrical properties.

## Conceptual Problems

1. Describe the common structural features of molecules that form liquid crystals. What kind of intermolecular interactions are most likely to result in a long-chain molecule that exhibits liquid crystalline behavior? Does an electrical field affect these interactions?
2. What is the difference between an *isotropic* liquid and an *anisotropic* liquid? Which is more anisotropic—a cholesteric liquid crystal or a nematic liquid crystal?

## Contributors

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# 11.9: Essential Skills 6

**Learning Objectives**

- Natural Logarithms
- Calculations Using Natural Logarithms

Essential Skills 3 in Section 4.11, introduced the common, or base-10, logarithms and showed how to use the properties of exponents to perform logarithmic calculations. In this section, we describe natural logarithms, their relationship to common logarithms, and how to do calculations with them using the same properties of exponents.

## Natural Logarithms

Many natural phenomena exhibit an exponential rate of increase or decrease. Population growth is an example of an exponential rate of increase, whereas a runner's performance may show an exponential decline if initial improvements are substantially greater than those that occur at later stages of training. Exponential changes are represented logarithmically by $e^x$, where $e$ is an irrational number whose value is approximately 2.7183. The *natural logarithm*, abbreviated as ln, is the power $x$ to which $e$ must be raised to obtain a particular number. The natural logarithm of $e$ is 1 ($\ln e = 1$).

Some important relationships between base-10 logarithms and natural logarithms are as follows:

$10^1 = 10 = e^{2.303}$ $\ln e^x = x \ln 10 = \ln(e^{2.303}) = 2.303 \log 10 = \ln e = 1$

According to these relationships, $\ln 10 = 2.303$ and $\log 10 = 1$. Because multiplying by 1 does not change an equality,

$\ln 10 = 2.303 \log 10$

Substituting any value $y$ for 10 gives

$\ln y = 2.303 \log y$

Other important relationships are as follows:

$\log A^x = x \log A$ $\ln e^x = x \ln e = x = e^{\ln x}$

Entering a value $x$, such as 3.86, into your calculator and pressing the "ln" key gives the value of $\ln x$, which is 1.35 for $x = 3.86$. Conversely, entering the value 1.35 and pressing "$e^x$" key gives an answer of 3.86.On some calculators, pressing [INV] and then [ln $x$] is equivalent to pressing [$ex$]. Hence

$e^{\ln 3.86} = e^{1.35} = 3.86$ $\ln(e^{3.86}) = 3.86$

### Skill Builder ES1

Calculate the natural logarithm of each number and express each as a power of the base $e$.

1. 0.523
2. 1.63

**Solution:**

1. $\ln(0.523) = -0.648$; $e^{-0.648} = 0.523$
2. $\ln(1.63) = 0.489$; $e^{0.489} = 1.63$

### Skill Builder ES2

What number is each value the natural logarithm of?

1. 2.87
2. 0.030
3. −1.39

**Solution:**

1. $\ln x = 2.87$; $x = e^{2.87} = 17.6 = 18$ to two significant figures

2. ln $x$ = 0.030; $x = e^{0.030}$ = 1.03 = 1.0 to two significant figures
3. ln $x$ = −1.39; $x = e^{-1.39}$ = 0.249 = 0.25

## Calculations with Natural Logarithms

Like common logarithms, natural logarithms use the properties of exponents. We can compare the properties of common and natural logarithms:

| Operation | Exponential Form | Logarithm |
|---|---|---|
| Multiplication | $(10^a)(10^b) = 10^{a+b}$ | $\log(ab) = \log a + \log b$ |
| | $(e^x)(e^y) = e^{x+y}$ | $\ln(e^x e^y) = \ln(e^x) + \ln(e^y) = x + y$ |
| Division | $\frac{10^a}{10^b} = 10^{a-b}$<br>$\frac{e^a}{e^b} = e^{a-b}$ | $log\left(\frac{a}{b}\right) = log\ a - log\ b$<br>$ln\left(\frac{x}{y}\right) = ln\ x - ln\ y$<br>$ln\left(\frac{e^x}{e^y}\right) = ln\,(e^x) - ln\,(e^y) = x - y$ |
| Inverse | | $log\left(\frac{1}{a}\right) = -log\,(a)$<br>$ln\left(\frac{1}{x}\right) = -ln\,(x)$ |

The number of significant figures in a number is the same as the number of digits after the decimal point in its logarithm. For example, the natural logarithm of 18.45 is 2.9151, which means that $e^{2.9151}$ is equal to 18.45.

### Skill Builder ES3

Calculate the natural logarithm of each number.

1. 22 × 18.6
2. $\frac{0.51}{2.67}$
3. 0.079 × 1.485
4. $\frac{20.5}{0.026}$

**Solution:**

1. ln(22 × 18.6) = ln(22) + ln(18.6) = 3.09 + 2.923 = 6.01. Alternatively, 22 × 18.6 = 410; ln(410) = 6.02.
2. $ln\left(\frac{0.51}{2.67}\right) = ln\,(0.51) - ln\,(2.67) = -0.67 - 0.982 = -1.65$ ln(0.19) = −1.66.
3. ln(0.079 × 1.485) = ln(0.079) + ln(1.485) = −2.54 + 0.395 = −2.15. Alternatively, 0.079 × 1.485 = 0.12; ln(0.12) = −2.12.
4. $ln\left(\frac{20.5}{0.026}\right) = ln\,(20.5) - ln\,(0.026) = 3.0204 - (-3.65) = 6.67$ ln(790) = 6.67.

The answers obtained using the two methods may differ slightly due to rounding errors.

### Skill Builder ES4

Calculate the natural logarithm of each number.

1. 34 × 16.5
2. 2.10/0.052
3. 0.402 × 3.930

4. 0.164/10.7

**Solution:**

1. 6.33
2. 3.70
3. 0.457
4. −4.178

## Contributors

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# CHAPTER OVERVIEW

## 12: Solids

In this chapter, we turn our attention to the structures and properties of solids. The solid state is distinguished from the gas and liquid states by a rigid structure in which the component atoms, ions, or molecules are usually locked into place. In many solids, the components are arranged in extended three-dimensional patterns, producing a wide range of properties that can often be tailored to specific functions. Thus diamond, an allotrope of elemental carbon, is one of the hardest materials known, yet graphite, another allotrope of carbon, is a soft, slippery material used in pencil lead and as a lubricant. Metallic sodium is soft enough to be cut with a dull knife, but crystalline sodium chloride turns into a fine powder when struck with a hammer.


12.1: Crystalline and Amorphous Solids
12.2: The Arrangement of Atoms in Crystalline Solids
12.3: Structures of Simple Binary Compounds
12.4: Defects in Crystals
12.5: Bonding and Properties of Solids
12.6: Metals and Semiconductors
12.7: Superconductors
12.8: Polymers
12.9: Modern Materials


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# 12.1: Crystalline and Amorphous Solids

**Learning Objectives**

- To understand the difference between a crystalline and an amorphous solid

Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays. The learning objective of this module is to know the characteristic properties of crystalline and amorphous solids.

## Introduction

With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the positions of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal lattice, thus producing a crystalline solid, or they can aggregate with no particular order, in which case they form an amorphous solid (from the Greek ámorphos, meaning “shapeless”).




***(left) Crystalline faces**. The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite ($FeS_2$), or at other angles, as in quartz.*(Right) ***Cleavage surfaces of an amorphous solid**. Obsidian, a volcanic glass with the same chemical composition as granite (typically $KAlSi_3O_8$), tends to have curved, irregular surfaces when cleaved.*

Crystalline solids, or crystals, have distinctive internal structures that in turn lead to distinctive flat surfaces, or faces. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material. The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure 12.1), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.

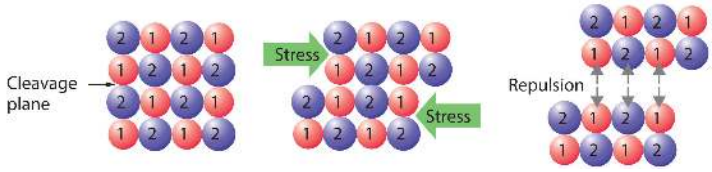
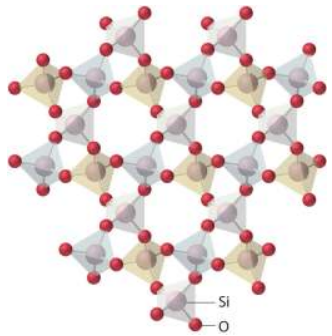



Figure 12.1: Cleaving a Crystal of an Ionic Compound along a Plane of Ions. Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local

environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glass. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are $SiO_2$ and both consist of linked $SiO_4$ tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten $SiO_2$ is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of $4 \times 10^{13}$ K/s, which prevents the atoms from arranging themselves into a regular array.




***The lattice of crystalline quartz ($SiO_2$).*** *The atoms form a regular arrangement in a structure that consists of linked tetrahedra.*

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

| Note |
| --- |
| Crystals have sharp, well-defined melting points; amorphous solids do not. |

## Summary

Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a crystal lattice), which results in a crystalline solid, or more or less randomly to produce an amorphous solid. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

## Conceptual Problems

1. Compare the solid and liquid states in terms of

    a. rigidity of structure.

    b. long-range order.

    c. short-range order.

2. How do amorphous solids differ from crystalline solids in each characteristic? Which of the two types of solid is most similar to a liquid?

a. rigidity of structure

b. long-range order

c. short-range order

3. Why is the arrangement of the constituent atoms or molecules more important in determining the properties of a solid than a liquid or a gas?

4. Why are the structures of solids usually described in terms of the positions of the constituent atoms rather than their motion?

5. What physical characteristics distinguish a crystalline solid from an amorphous solid? Describe at least two ways to determine experimentally whether a material is crystalline or amorphous.

6. Explain why each characteristic would or would not favor the formation of an amorphous solid.

a. slow cooling of pure molten material

b. impurities in the liquid from which the solid is formed

c. weak intermolecular attractive forces

7. A student obtained a solid product in a laboratory synthesis. To verify the identity of the solid, she measured its melting point and found that the material melted over a 12°C range. After it had cooled, she measured the melting point of the same sample again and found that this time the solid had a sharp melting point at the temperature that is characteristic of the desired product. Why were the two melting points different? What was responsible for the change in the melting point?

## Conceptual Answers

3. The arrangement of the atoms or molecules is more important in determining the properties of a solid because of the greater persistent long-range order of solids. Gases and liquids cannot readily be described by the spatial arrangement of their components because rapid molecular motion and rearrangement defines many of the properties of liquids and gases.

7. The initial solid contained the desired compound in an amorphous state, as indicated by the wide temperature range over which melting occurred. Slow cooling of the liquid caused it to crystallize, as evidenced by the sharp second melting point observed at the expected temperature.

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# 12.2: The Arrangement of Atoms in Crystalline Solids

**Learning Objectives**

- To recognize the unit cell of a crystalline solid.
- To calculate the density of a solid given its unit cell.

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a crystal lattice), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cell. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure 12.2. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in part (d) in Figure 12.2 is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure 12.3.

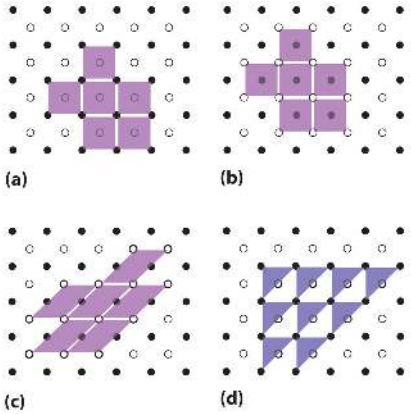



Figure 12.2 Unit Cells in Two Dimensions. *(a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern. (CC BY-NC-SA; anonymous by request)*

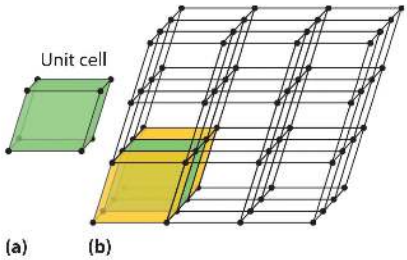



Figure 12.3 Unit Cells in Three Dimensions. *These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice. (CC BY-NC-SA; anonymous by request)*

## The Unit Cell

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure 12.4). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in which all sides have the same length and all angles are 90°, but the concepts that we introduce also apply to substances whose unit cells are not cubic.

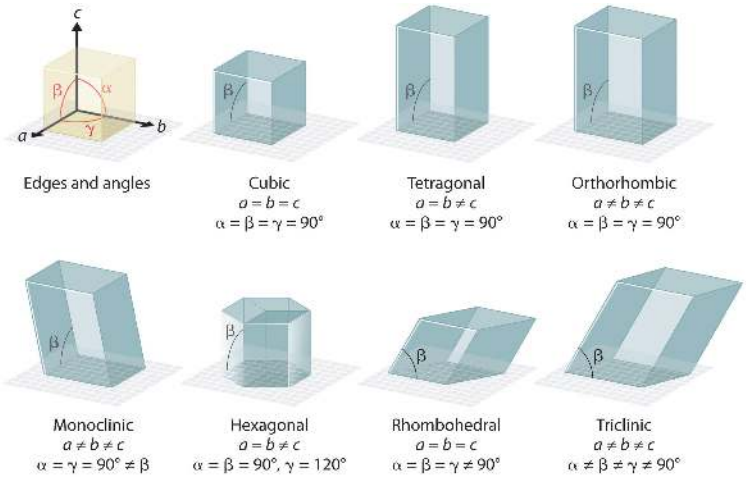



Figure 12.4 The General Features of the Seven Basic Unit Cells. *The lengths of the edges of the unit cells are indicated by a, b, and c, and the angles are defined as follows: α, the angle between b and c; β, the angle between a and c; and γ, the angle between a and b. (CC BY-NC-SA; anonymous by request)*

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubic (part (a) in Figure 12.5). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc) (part (b) in Figure 12.5). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc) (part (c) in Figure 12.5).

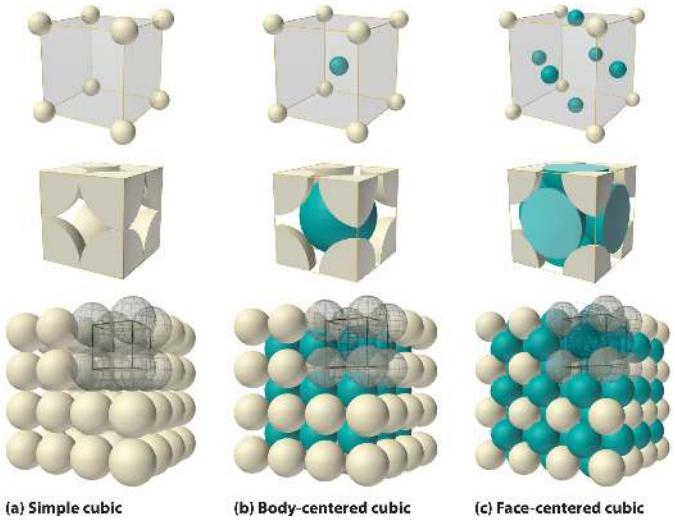



Figure 12.5 The Three Kinds of Cubic Unit Cell. *For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells. (CC BY-NC-SA; anonymous by request)*

As indicated in Figure 12.5, a solid consists of a large number of unit cells arrayed in three dimensions. Any intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because density is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 12.5. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore counted as 12 atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes 14 atom to each. An atom at a corner of a unit cell is shared by all eight adjacent unit cells and therefore contributes 18 atom to each.The statement that atoms lying on an edge or a corner of a unit cell count as 14 or 18 atom per unit cell, respectively, is true for all unit cells except the hexagonal one, in which three unit cells share each vertical edge and six share each corner

(Figure 12.4), leading to values of 13 and 16 atom per unit cell, respectively, for atoms in these positions. In contrast, atoms that lie entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

Note

For all unit cells except hexagonal, atoms on the faces contribute $\frac{1}{2}$ atom to each unit cell, atoms on the edges contribute $\frac{1}{4}$ atom to each unit cell, and atoms on the corners contribute $\frac{1}{8}$ atom to each unit cell.

Example 1

Metallic gold has a face-centered cubic unit cell (part (c) in Figure 12.5). How many Au atoms are in each unit cell?
**Given**: unit cell
**Asked for**: number of atoms per unit cell
**Strategy**:
Using Figure 12.5, identify the positions of the Au atoms in a face-centered cubic unit cell and then determine how much each Au atom contributes to the unit cell. Add the contributions of all the Au atoms to obtain the total number of Au atoms in a unit cell.
**Solution**:
As shown in Figure 12.5, a face-centered cubic unit cell has eight atoms at the corners of the cube and six atoms on the faces. Because atoms on a face are shared by two unit cells, each counts as $\frac{1}{2}$ atom per unit cell, giving $6\times\frac{1}{2}=3$ Au atoms per unit cell. Atoms on a corner are shared by eight unit cells and hence contribute only $\frac{1}{8}$ atom per unit cell, giving $8\times\frac{1}{8}=1$ Au atom per unit cell. The total number of Au atoms in each unit cell is thus 3 + 1 = 4.

Exercise 1

Metallic iron has a body-centered cubic unit cell (part (b) in Figure 12.5). How many Fe atoms are in each unit cell?
**Answer**: two

Now that we know how to count atoms in unit cells, we can use unit cells to calculate the densities of simple compounds. Note, however, that we are assuming a solid consists of a perfect regular array of unit cells, whereas real substances contain impurities and defects that affect many of their bulk properties, including density. Consequently, the results of our calculations will be close but not necessarily identical to the experimentally obtained values.

Example 2

Calculate the density of metallic iron, which has a body-centered cubic unit cell (part (b) in Figure 12.5) with an edge length of 286.6 pm.

**Given**: unit cell and edge length

**Asked for**: density

**Strategy**:

A. Determine the number of iron atoms per unit cell.

B. Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro's number. Then divide the mass by the volume of the cell.

**Solution**:

**A** We know from Example 1 that each unit cell of metallic iron contains two Fe atoms.

**B** The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro's number and then divide the mass by the volume of the cell (making sure to use suitable units to get density in g/cm$^3$):

$$mass\ of\ Fe = (2\ \cancel{atoms}\ Fe)\left(\frac{1\ \cancel{mol}}{6.022\times10^{23}\ \cancel{atoms}}\right)\left(\frac{55.85\ g}{\cancel{mol}}\right) = 1.855\times10^{-22}\ g \tag{12.2.1}$$

$$volume = \left[(286.6\ pm)\left(\frac{10^{-12}\ \cancel{m}}{\cancel{pm}}\right)\left(\frac{10^{2}\ cm}{\cancel{m}}\right)\right] = 2.345\times10^{-23}\ cm^3 \tag{12.2.2}$$

$$density = \frac{1.855\times10^{-22}\ g}{2.345\times10^{-23}\ cm^3} = 7.880 g/cm^3 \tag{12.2.3}$$

This result compares well with the tabulated experimental value of 7.874 g/cm$^3$.

Exercise

Calculate the density of gold, which has a face-centered cubic unit cell (part (c) in Figure 12.5) with an edge length of 407.8 pm.

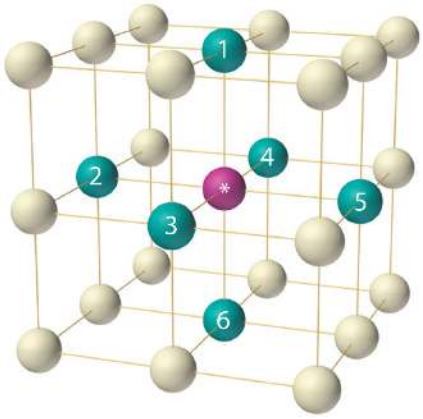
**Answer**: 19.29 g/cm$^3$

## Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

## Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in part (a) in Figure 12.5. Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa.




***The arrangement of atoms in a simple cubic unit cell**. Each atom in the lattice has six nearest neighbors in an octahedral arrangement.*

## Body-Centered Cubic Structure

The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in part (b) in Figure 12.5, the body-centered cubic structure consists of a single layer of spheres in contact with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped “holes” above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

## Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in part (a) in Figure 12.6. Each sphere is surrounded by six others in the same plane to produce a hexagonal arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be divided into two sets, labeled B and C in part (a) in Figure 12.6. Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

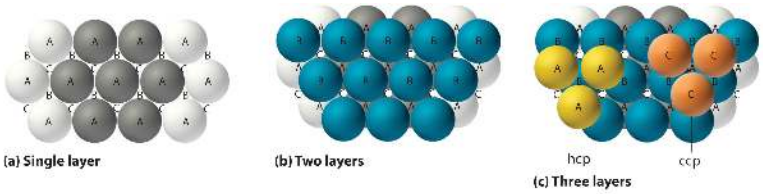



Figure 12.6: Close-Packed Layers of Spheres. *(a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms at A positions in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure. (CC BY-NC-SA; anonymous by request)*

If we place the second layer of spheres at the B positions in part (a) in Figure 12.6, we obtain the two-layered structure shown in part (b) in Figure 12.6. There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did not use for the atoms in the first or second layers (part (c) in Figure 12.6). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB…, resulting in a hexagonal close-packed (hcp) structure (part (a) in Figure 12.7). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC…, giving a cubic close-packed (ccp) structure (part (b) in Figure 12.7). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in part (b) in Figure 12.7, however, simply

rotating the structure reveals its cubic nature, which is identical to a fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

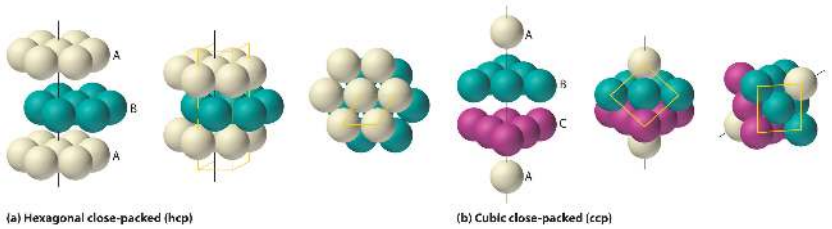



Figure 12.7 Close-Packed Structures: hcp and ccp. The illustrations in (a) show an exploded view, a side view, and a top view of the hcp structure. The simple hexagonal unit cell is outlined in the side and top views. Note the similarity to the hexagonal unit cell shown in Figure 12.4. The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube. *(CC BY-NC-SA; anonymous by request)*

Table 12.1 compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination number. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

**Table 12.1:** Properties of the Common Structures of Metals

| Structure | Percentage of Space Occupied by Atoms | Coordination Number |
|---|---|---|
| simple cubic | 52 | 6 |
| body-centered cubic | 68 | 8 |
| hexagonal close packed | 74 | 12 |
| cubic close packed (identical to face-centered cubic) | 74 | 12 |

## Summary

The smallest repeating unit of a crystal lattice is the unit cell. The simple cubic unit cell contains only eight atoms, molecules, or ions at the corners of a cube. A body-centered cubic (bcc) unit cell contains one additional component in the center of the cube. A face-centered cubic (fcc) unit cell contains a component in the center of each face in addition to those at the corners of the cube. Simple cubic and bcc arrangements fill only 52% and 68% of the available space with atoms, respectively. The hexagonal close-packed (hcp) structure has an ABABAB… repeating arrangement, and the cubic close-packed (ccp) structure has an ABCABC… repeating pattern; the latter is identical to an fcc lattice. The hcp and ccp arrangements fill 74% of the available space and have a coordination number of 12 for each atom in the lattice, the number of nearest neighbors. The simple cubic and bcc lattices have coordination numbers of 6 and 8, respectively.

## Key Takeaway

A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure.

## Conceptual Problems

1. Why is it valid to represent the structure of a crystalline solid by the structure of its unit cell? What are the most important constraints in selecting a unit cell?

2. All unit cell structures have six sides. Can crystals of a solid have more than six sides? Explain your answer.

3. Explain how the intensive properties of a material are reflected in the unit cell. Are all the properties of a bulk material the same as those of its unit cell? Explain your answer.

4. The experimentally measured density of a bulk material is slightly higher than expected based on the structure of the pure material. Propose two explanations for this observation.

5. The experimentally determined density of a material is lower than expected based on the arrangement of the atoms in the unit cell, the formula mass, and the size of the atoms. What conclusion(s) can you draw about the material?

6. Only one element (polonium) crystallizes with a simple cubic unit cell. Why is polonium the only example of an element with this structure?

7. What is meant by the term coordination number in the structure of a solid? How does the coordination number depend on the structure of the metal?

8. Arrange the three types of cubic unit cells in order of increasing packing efficiency. What is the difference in packing efficiency between the hcp structure and the ccp structure?

9. The structures of many metals depend on pressure and temperature. Which structure—bcc or hcp—would be more likely in a given metal at very high pressures? Explain your reasoning.

10. A metal has two crystalline phases. The transition temperature, the temperature at which one phase is converted to the other, is 95°C at 1 atm and 135°C at 1000 atm. Sketch a phase diagram for this substance. The metal is known to have either a ccp structure or a simple cubic structure. Label the regions in your diagram appropriately and justify your selection for the structure of each phase.

## Numerical Problems

1. Metallic rhodium has an fcc unit cell. How many atoms of rhodium does each unit cell contain?

2. Chromium has a structure with two atoms per unit cell. Is the structure of this metal simple cubic, bcc, fcc, or hcp?

3. The density of nickel is 8.908 g/cm$^3$. If the metallic radius of nickel is 125 pm, what is the structure of metallic nickel?

4. The density of tungsten is 19.3 g/cm$^3$. If the metallic radius of tungsten is 139 pm, what is the structure of metallic tungsten?

5. An element has a density of 10.25 g/cm$^3$ and a metallic radius of 136.3 pm. The metal crystallizes in a bcc lattice. Identify the element.

6. A 21.64 g sample of a nonreactive metal is placed in a flask containing 12.00 mL of water; the final volume is 13.81 mL. If the length of the edge of the unit cell is 387 pm and the metallic radius is 137 pm, determine the packing arrangement and identify the element.

7. A sample of an alkali metal that has a bcc unit cell is found to have a mass of 1.000 g and a volume of 1.0298 cm$^3$. When the metal reacts with excess water, the reaction produces 539.29 mL of hydrogen gas at 0.980 atm and 23°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.

8. A sample of an alkaline earth metal that has a bcc unit cell is found to have a mass 5.000 g and a volume of 1.392 cm$^3$. Complete reaction with chlorine gas requires 848.3 mL of chlorine gas at 1.050 atm and 25°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.

9. Lithium crystallizes in a bcc structure with an edge length of 3.509 Å. Calculate its density. What is the approximate metallic radius of lithium in picometers?

10. Vanadium is used in the manufacture of rust-resistant vanadium steel. It forms bcc crystals with a density of 6.11 g/cm$^3$ at 18.7°C. What is the length of the edge of the unit cell? What is the approximate metallic radius of the vanadium in picometers?

11. A simple cubic cell contains one metal atom with a metallic radius of 100 pm.

    a. Determine the volume of the atom(s) contained in one unit cell [the volume of a sphere = $(\frac{4}{3})\pi r^3$].

    b. What is the length of one edge of the unit cell? (Hint: there is no empty space between atoms.)

    c. Calculate the volume of the unit cell.

    d. Determine the packing efficiency for this structure.

e. Use the steps in Problem 11 to calculate the packing efficiency for a bcc unit cell with a metallic radius of 1.00 Å.

## Numerical Answers

1. four

3. fcc

5. molybdenum

7. sodium, unit cell edge = 428 pm, r = 185 pm

9. d = 0.5335 g/cm$^3$, r =151.9 pm

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# 12.3: Structures of Simple Binary Compounds

**Learning Objectives**

- To use the cation:anion radius ratio to predict the structures of simple binary compounds.
- To understand how x-rays are diffracted by crystalline solids.

The structures of most binary compounds can be described using the packing schemes we have just discussed for metals. To do so, we generally focus on the arrangement in space of the largest species present. In ionic solids, this generally means the anions, which are usually arranged in a simple cubic, bcc, fcc, or hcp lattice. Often, however, the anion lattices are not truly "close packed"; because the cations are large enough to prop them apart somewhat, the anions are not actually in contact with one another. In ionic compounds, the cations usually occupy the "holes" between the anions, thus balancing the negative charge. The ratio of cations to anions within a unit cell is required to achieve electrical neutrality and corresponds to the bulk stoichiometry of the compound.

## Common Structures of Binary Compounds

As shown in part (a) in Figure 12.8, a simple cubic lattice of anions contains only one kind of hole, located in the center of the unit cell. Because this hole is equidistant from all eight atoms at the corners of the unit cell, it is called a cubic hole. An atom or ion in a cubic hole therefore has a coordination number of 8.

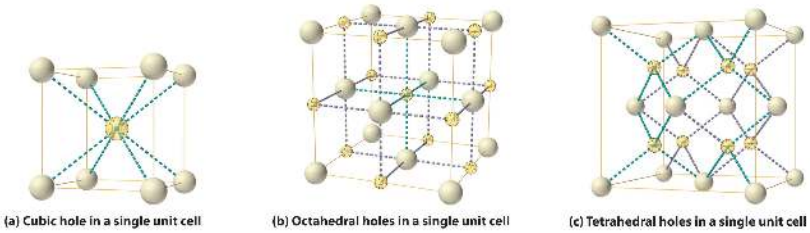



Figure 12.8 Holes in Cubic Lattices. *The three illustrations show (a) the cubic hole that is in the center of a simple cubic lattice of anions, (b) the locations of the octahedral holes in a face-centered cubic lattice of anions, and (c) the locations of the tetrahedral holes in a face-centered cubic lattice of anions.*

Many ionic compounds with relatively large cations and a 1:1 cation:anion ratio have this structure, which is called the cesium chloride structure (Figure 12.9) because CsCl is a common example.Solid-state chemists tend to describe the structures of new compounds in terms of the structure of a well-known reference compound. Hence you will often read statements such as "Compound X possesses the cesium chloride (or sodium chloride, etc.) structure" to describe the structure of compound X. Notice in Figure 12.9 that the z = 0 and the z = 1.0 planes are always the same. This is because the z = 1.0 plane of one unit cell becomes the z = 0 plane of the succeeding one. The unit cell in CsCl contains a single Cs+ ion as well as 8×18Cl−=1Cl− ion, for an overall stoichiometry of CsCl. The cesium chloride structure is most common for ionic substances with relatively large cations, in which the ratio of the radius of the cation to the radius of the anion is in the range shown in Table 12.2.

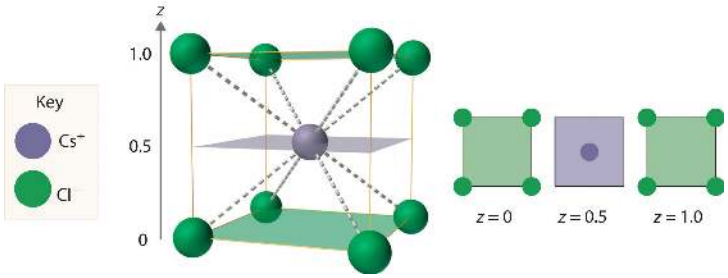



Figure 12.9: The Cesium Chloride Structure. *The Cs+ ion occupies the cubic hole in the center of a cube of Cl− ions. The drawings at the right are horizontal cross-sections through the unit cell at the bottom (z = 0) and halfway between the bottom and top (z = 0.5). A top cross-section (z = 1) is identical to z = 0. Such cross-sections often help us visualize the arrangement of atoms or ions in the unit cell more easily.*

**Table 12.2** Relationship between the Cation:Anion Radius Ratio and the Site Occupied by the Cations

| Approximate Range of Cation:Anion Radius Ratio | Hole Occupied by Cation | Cation Coordination Number |
|---|---|---|
| 0.225–0.414 | tetrahedral | 4 |
| 0.414–0.732 | octahedral | 6 |
| 0.732–1.000 | cubic | 8 |

| Note |
|---|
| Very large cations occupy cubic holes, cations of intermediate size occupy octahedral holes, and small cations occupy tetrahedral holes in the anion lattice. |

In contrast, a face-centered cubic (fcc) array of atoms or anions contains two types of holes: octahedral holes, one in the center of the unit cell plus a shared one in the middle of each edge (part (b) in Figure 12.8), and tetrahedral holes, located between an atom at a corner and the three atoms at the centers of the adjacent faces (part (c) in Figure 12.8). As shown in Table 12.2, the ratio of the radius of the cation to the radius of the anion is the most important determinant of whether cations occupy the cubic holes in a cubic anion lattice or the octahedral or tetrahedral holes in an fcc lattice of anions. Very large cations occupy cubic holes in a cubic anion lattice, cations of intermediate size tend to occupy the octahedral holes in an fcc anion lattice, and relatively small cations tend to occupy the tetrahedral holes in an fcc anion lattice. In general, larger cations have higher coordination numbers than small cations.

The most common structure based on a fcc lattice is the sodium chloride structure (Figure 12.10), which contains an fcc array of $Cl^-$ ions with $Na^+$ ions in all the octahedral holes. We can understand the sodium chloride structure by recognizing that filling all the octahedral holes in an fcc lattice of $Cl^-$ ions with $Na^+$ ions gives a total of 4 $Cl^-$ ions (one on each face gives $6\times \frac{1}{2}=3$ plus one on each corner gives $8\times \frac{1}{8}=1$, for a total of 4) and 4 $Na^+$ ions (one on each edge gives $12\times\frac{1}{4}=3$ plus one in the middle, for a total of 4). The result is an electrically neutral unit cell and a stoichiometry of NaCl. As shown in Figure 12.10, the $Na^+$ ions in the sodium chloride structure also form an fcc lattice. The sodium chloride structure is favored for substances with two atoms or ions in a 1:1 ratio and in which the ratio of the radius of the cation to the radius of the anion is between 0.414 and 0.732. It is observed in many compounds, including MgO and TiC.

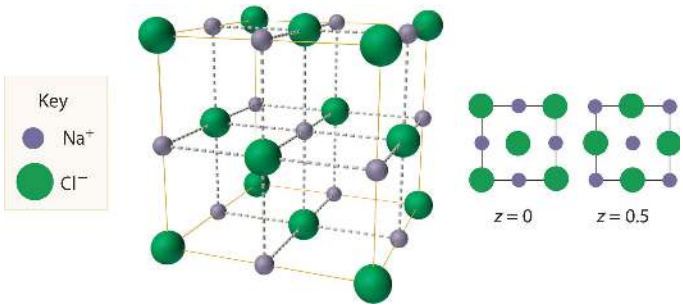



Figure 12.10 The Sodium Chloride Structure. *In NaCl, the $Na^+$ ions occupy the octahedral holes in an fcc lattice of $Cl^-$ ions, resulting in an fcc array of $Na^+$ ions as well.*

The structure shown in Figure 12.11 is called the zinc blende structure, from the common name of the mineral ZnS. It results when the cation in a substance with a 1:1 cation:anion ratio is much smaller than the anion (if the cation:anion radius ratio is less than about 0.414). For example, ZnS contains an fcc lattice of $S^{2-}$ ions, and the cation:anion radius ratio is only about 0.40, so we predict that the cation would occupy either a tetrahedral hole or an octahedral hole. In fact, the relatively small $Zn^{2+}$ cations occupy the tetrahedral holes in the lattice. If all 8 tetrahedral holes in the unit cell were occupied by $Zn^{2+}$ ions, however, the unit cell would contain 4 $S^{2-}$ and 8 $Zn^{2+}$ ions, giving a formula of $Zn_2S$ and a net charge of +4 per unit cell. Consequently, the $Zn^{2+}$ ions occupy every other tetrahedral hole, as shown in Figure 12.11, giving a total of 4 $Zn^{2+}$ and 4 $S^{2-}$ ions per unit cell and a formula of ZnS. The zinc blende structure results in a coordination number of 4 for each $Zn^{2+}$ ion and a tetrahedral arrangement of the four $S^{2-}$ ions around each $Zn^{2+}$ ion.

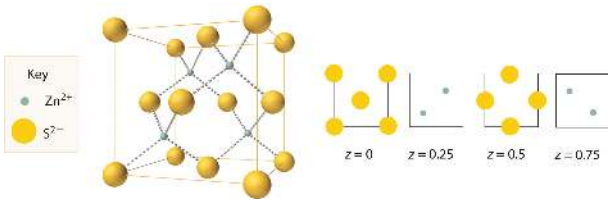



Figure 12.11 The Zinc Blende Structure. *$Zn^{2+}$ ions occupy every other tetrahedral hole in the fcc array of $S^{2-}$ ions. Each $Zn^{2+}$ ion is surrounded by four $S^{2-}$ ions in a tetrahedral arrangement.*

Example 3

a. If all the tetrahedral holes in an fcc lattice of anions are occupied by cations, what is the stoichiometry of the resulting compound?
b. Use the ionic radii given in Figure 7.9 to identify a plausible oxygen-containing compound with this stoichiometry and structure.
**Given**: lattice, occupancy of tetrahedral holes, and ionic radii
**Asked for**: stoichiometry and identity
**Strategy**:
A. Use Figure 12.8 to determine the number and location of the tetrahedral holes in an fcc unit cell of anions and place a cation in each.
B. Determine the total number of cations and anions in the unit cell; their ratio is the stoichiometry of the compound.
C. From the stoichiometry, suggest reasonable charges for the cation and the anion. Use the data in Figure 7.9 to identify a cation–anion combination that has a cation:anion radius ratio within a reasonable range.
**Solution**:
a**. A** Figure 12.8 shows that the tetrahedral holes in an fcc unit cell of anions are located entirely within the unit cell, for a total of eight (one near each corner). **B** Because the tetrahedral holes are located entirely within the unit cell, there are eight cations per unit cell. We calculated previously that an fcc unit cell of anions contains a total of four anions per unit cell. The stoichiometry of the compound is therefore $M_8Y_4$ or, reduced to the smallest whole numbers, $M_2Y$.
b. **C** The $M_2Y$ stoichiometry is consistent with a lattice composed of $M^+$ ions and $Y^{2-}$ ions. If the anion is $O^{2-}$ (ionic radius 140 pm), we need a monocation with a radius no larger than about 140 × 0.414 = 58 pm to fit into the tetrahedral holes. According to Figure 7.9, none of the monocations has such a small radius; therefore, the most likely possibility is $Li^+$ at 76 pm. Thus we expect $Li_2O$ to have a structure that is an fcc array of $O^{2-}$ anions with $Li^+$ cations in all the tetrahedral holes.

Exercise 1

If only half the octahedral holes in an fcc lattice of anions are filled by cations, what is the stoichiometry of the resulting compound?
**Answer**: $MX_2$; an example of such a compound is cadmium chloride ($CdCl_2$), in which the empty cation sites form planes running through the crystal.

We examine only one other structure of the many that are known, the perovskite structure. Perovskite is the generic name for oxides with two different kinds of metal and have the general formula $MM'O_3$, such as $CaTiO_3$. The structure is a body-centered cubic (bcc) array of two metal ions, with one M (Ca in this case) located at the corners of the cube, and the other M′ (in this case Ti) in the centers of the cube. The oxides are in the centers of the square faces (part (a) in Figure 12.12). The stoichiometry predicted from the unit cell shown in part (a) in Figure 12.12 agrees with the general formula; each unit cell contains $8\times \frac{1}{8} = 1$ Ca, 1 Ti, and $6\times \frac{1}{2} = 3$ O atoms. The Ti and Ca atoms have coordination numbers of 6 and 12, respectively. We will return to the perovskite structure when we discuss high-temperature superconductors in Section 12.7.

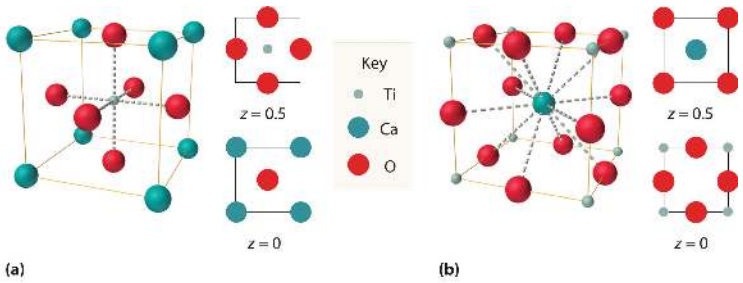



Figure 12.12 The Perovskite Structure of $CaTiO_3$. *Two equivalent views are shown: (a) a view with the Ti atom at the center and (b) an alternative view with the Ca atom at the center.*

## X-Ray Diffraction

As you learned in Chapter 6, the wavelengths of x-rays are approximately the same magnitude as the distances between atoms in molecules or ions. Consequently, x-rays are a useful tool for obtaining information about the structures of crystalline substances. In a technique called x-ray diffraction, a beam of x-rays is aimed at a sample of a crystalline material, and the x-rays are diffracted by layers of atoms in the crystalline lattice (part (a) in Figure 12.13). When the beam strikes photographic film, it produces an x-ray diffraction pattern, which consists of dark spots on a light background (part (b) in Figure 12.13). In 1912, the German physicist Max von Laue (1879–1960; Nobel Prize in Physics, 1914) predicted that x-rays should be diffracted by crystals, and his prediction was rapidly confirmed. Within a year, two British physicists, William Henry Bragg (1862–1942) and his son, William Lawrence Bragg (1890–1972), had worked out the mathematics that allows x-ray diffraction to be used to measure interatomic distances in crystals. The Braggs shared the Nobel Prize in Physics in 1915, when the son was only 25 years old. Virtually everything we know today about the detailed structures of solids and molecules in solids is due to the x-ray diffraction technique.

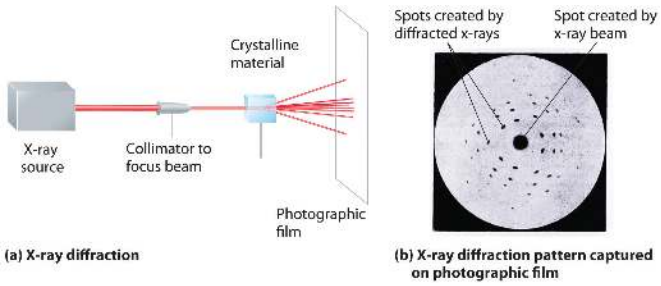



Figure 12.13 X-Ray Diffraction. *These illustrations show (a) a schematic drawing of x-ray diffraction and (b) the x-ray diffraction pattern of a zinc blende crystalline solid captured on photographic film.*

Recall from Chapter 6 that two waves that are in phase interfere constructively, thus reinforcing each other and generating a wave with a greater amplitude. In contrast, two waves that are out of phase interfere destructively, effectively canceling each other. When x-rays interact with the components of a crystalline lattice, they are scattered by the electron clouds associated with each atom. As shown in Figure 12.5, Figure 12.7, and Figure 12.8, the atoms in crystalline solids are typically arranged in planes. Figure 12.14 illustrates how two adjacent planes of atoms can scatter x-rays in a way that results in constructive interference. If two x-rays that are initially in phase are diffracted by two planes of atoms separated by a distance d, the lower beam travels the extra distance indicated by the lines BC and CD. The angle of incidence, designated as θ, is the angle between the x-ray beam and the planes in the crystal. Because BC = CD = d sin θ, the extra distance that the lower beam in Figure 12.14 must travel compared with the upper beam is 2d sin θ. For these two x-rays to arrive at a detector in phase, the extra distance traveled must be an integral multiple n of the wavelength λ:

$$2d \sin \theta = n\lambda \tag{12.1}$$

Equation 12.1 is the Bragg equation. The structures of crystalline substances with both small molecules and ions or very large biological molecules, with molecular masses in excess of 100,000 amu, can now be determined accurately and routinely using x-ray diffraction and the Bragg equation. Example 4 illustrates how to use the Bragg equation to calculate the distance between planes of atoms in crystals.

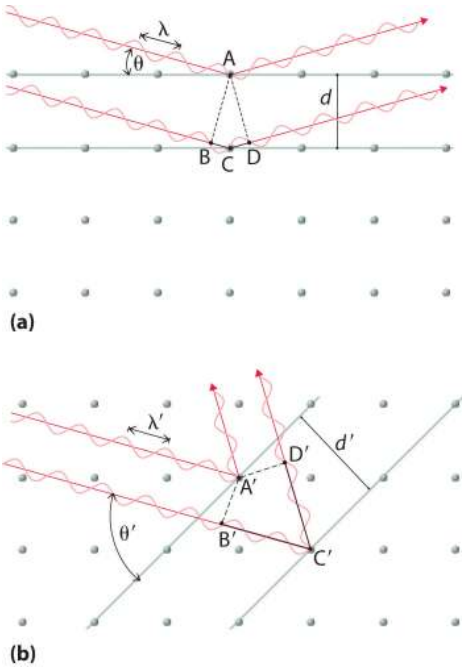



Figure 12.14 The Reflection of X-Rays from Two Adjacent Planes of Atoms Can Result in Constructive Interference of the X-Rays. *(a) The x-ray diffracted by the lower layer of atoms must travel a distance that is longer by 2d sin θ than the distance traveled by the x-ray diffracted by the upper layer of atoms. Only if this distance (BC plus CD) equals an integral number of wavelengths of the x-rays (i.e., only if λ = 2d sin θ) will the x-rays arrive at the detector in phase. (b) In a solid, many different sets of planes of atoms can diffract x-rays. Each has a different interplanar distance and therefore diffracts the x-rays at a different angle θ, which produces a characteristic pattern of spots.*

Example 4

X-rays from a copper x-ray tube (λ = 1.54062 Å or 154.062 pm)In x-ray diffraction, the angstrom (Å) is generally used as the unit of wavelength. are diffracted at an angle of 10.89° from a sample of crystalline gold. Assuming that n = 1, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to four significant figures.

**Given**: wavelength, diffraction angle, and number of wavelengths

**Asked for**: distance between planes

**Strategy**:

Substitute the given values into the Bragg equation and solve to obtain the distance between planes.

**Solution**:

We are given n, θ, and λ and asked to solve for d, so this is a straightforward application of the Bragg equation. For an answer in angstroms, we do not even have to convert units. Solving the Bragg equation for d gives

$$d = \frac{n\lambda}{2\sin\theta} \tag{12.3.1}$$

and substituting values gives

$$d = \frac{(1)(1.54062\,\overset{0}{A})}{2\,sin\,10.89^{0}} = 4.077\,\overset{0}{A} = 407.7\,pm \tag{12.3.2}$$

This value corresponds to the edge length of the fcc unit cell of elemental gold.

**Exercise**

X-rays from a molybdenum x-ray tube (λ = 0.709300 Å) are diffracted at an angle of 7.11° from a sample of metallic iron. Assuming that n = 1, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to three significant figures.

**Answer**: 2.87 Å or 287 pm (corresponding to the edge length of the bcc unit cell of elemental iron)

## Summary

The structures of most binary compounds are dictated by the packing arrangement of the largest species present (the anions), with the smaller species (the cations) occupying appropriately sized holes in the anion lattice. A simple cubic lattice of anions contains a single cubic hole in the center of the unit cell. Placing a cation in the cubic hole results in the cesium chloride structure, with a 1:1 cation:anion ratio and a coordination number of 8 for both the cation and the anion. An fcc array of atoms or ions contains both octahedral holes and tetrahedral holes. If the octahedral holes in an fcc lattice of anions are filled with cations, the result is a sodium chloride structure. It also has a 1:1 cation:anion ratio, and each ion has a coordination number of 6. Occupation of half the tetrahedral holes by cations results in the zinc blende structure, with a 1:1 cation:anion ratio and a coordination number of 4 for the cations. More complex structures are possible if there are more than two kinds of atoms in a solid. One example is the perovskite structure, in which the two metal ions form an alternating bcc array with the anions in the centers of the square faces. Because the wavelength of x-ray radiation is comparable to the interatomic distances in most solids, x-ray diffraction can be used to provide information about the structures of crystalline solids. X-rays diffracted from different planes of atoms in a solid reinforce one another if they are in phase, which occurs only if the extra distance they travel corresponds to an integral number of wavelengths. This relationship is described by the Bragg equation: 2d sin θ = nλ.

## Key Takeaway

- The ratio of cations to anions within a unit cell produces electrical neutrality and corresponds to the bulk stoichiometry of a compound, the structure of which can be determined using x-ray diffraction.

## Key Equation

**Bragg equation**

$$2d \sin \theta = n\lambda \tag{12.1}$$

## Conceptual Problems

1. Using circles or spheres, sketch a unit cell containing an octahedral hole. Which of the basic structural types possess octahedral holes? If an ion were placed in an octahedral hole, what would its coordination number be?

2. Using circles or spheres, sketch a unit cell containing a tetrahedral hole. Which of the basic structural types possess tetrahedral holes? If an ion were placed in a tetrahedral hole, what would its coordination number be?

3. How many octahedral holes are there in each unit cell of the sodium chloride structure? Potassium fluoride contains an fcc lattice of $F^-$ ions that is identical to the arrangement of $Cl^-$ ions in the sodium chloride structure. Do you expect $K^+$ ions to occupy the tetrahedral or octahedral holes in the fcc lattice of $F^-$ ions?

4. The unit cell of cesium chloride consists of a cubic array of chloride ions with a cesium ion in the center. Why then is cesium chloride described as having a simple cubic structure rather than a bcc structure? The unit cell of iron also consists of a cubic array of iron atoms with an iron atom in the center of the cube. Is this a bcc or a simple cubic unit cell? Explain your answer.

5. Why are x-rays used to determine the structure of crystalline materials? Could gamma rays also be used to determine crystalline structures? Why or why not?

6. X-rays are higher in energy than most other forms of electromagnetic radiation, including visible light. Why can’t you use visible light to determine the structure of a crystalline material?

7. When x-rays interact with the atoms in a crystal lattice, what relationship between the distances between planes of atoms in the crystal structure and the wavelength of the x-rays results in the scattered x-rays being exactly in phase with one another? What difference in structure between amorphous materials and crystalline materials makes it difficult to determine the structures of amorphous materials by x-ray diffraction?

8. It is possible to use different x-ray sources to generate x-rays with different wavelengths. Use the Bragg equation to predict how the diffraction angle would change if a molybdenum x-ray source (x-ray wavelength = 70.93 pm) were used instead of a copper source (x-ray wavelength = 154.1 pm).

9. Based on the Bragg equation, if crystal A has larger spacing in its diffraction pattern than crystal B, what conclusion can you draw about the spacing between layers of atoms in A compared with B?

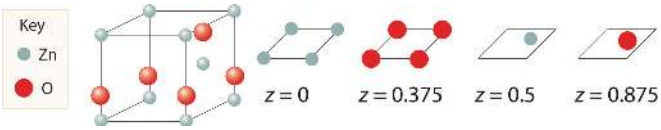
## Numerical Problems

1. Thallium bromide crystallizes in the cesium chloride structure. This bcc structure contains a $Tl^+$ ion in the center of the cube with $Br^-$ions at the corners. Sketch an alternative unit cell for this compound.

2. Potassium fluoride has a lattice identical to that of sodium chloride. The potassium ions occupy octahedral holes in an fcc lattice of fluoride ions. Propose an alternative unit cell that can also represent the structure of KF.

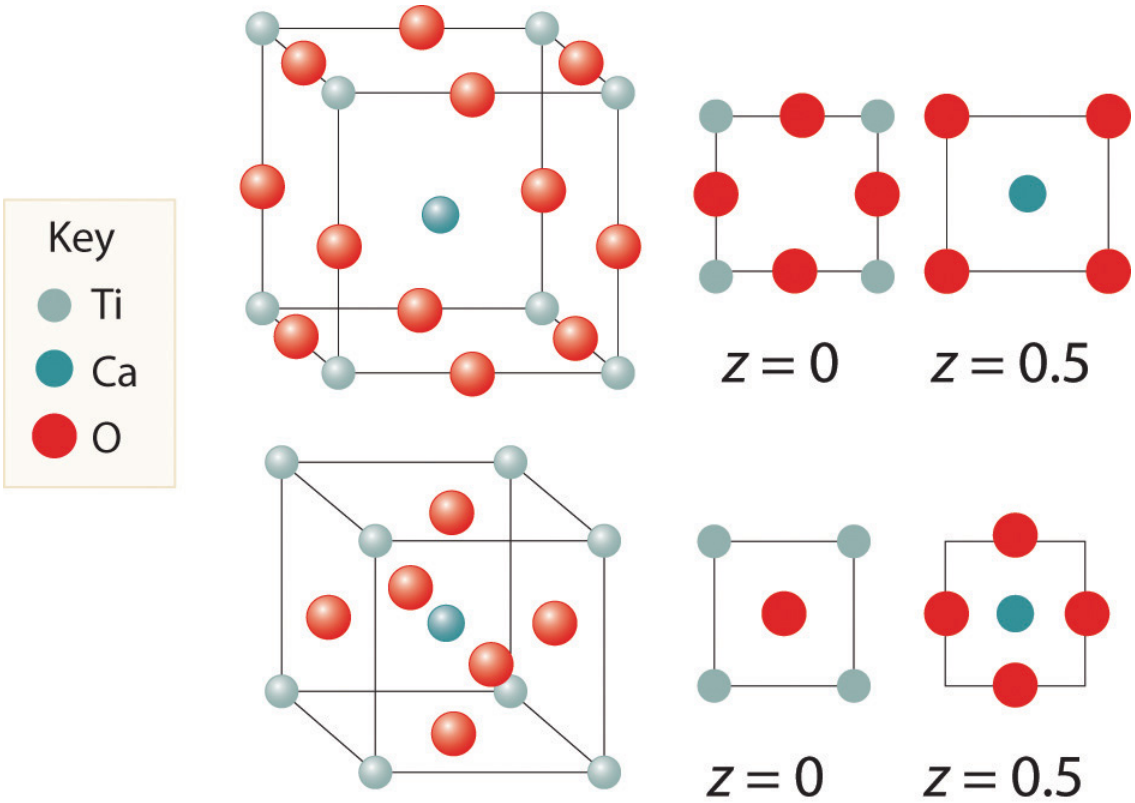
3. Calcium fluoride is used to fluoridate drinking water to promote dental health. Crystalline $CaF_2$ (d = 3.1805 g/cm$^3$) has a structure in which calcium ions are located at each corner and the middle of each edge of the unit cell, which contains eight fluoride ions per unit cell. The length of the edge of this unit cell is 5.463 Å. Use this information to determine Avogadro's number.

4. Zinc and oxygen form a compound that is used as both a semiconductor and a paint pigment. This compound has the following structure:




What is the empirical formula of this compound?

5. Here are two representations of the perovskite structure:



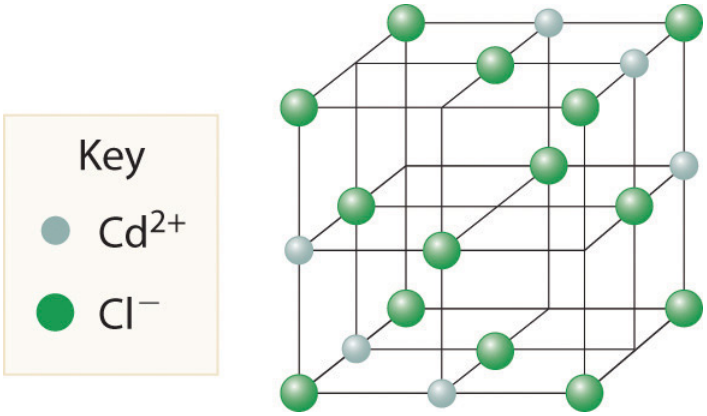

Are they identical? What is the empirical formula corresponding to each representation?

6. The salt $MX_2$ has a cubic close-packed (ccp) structure in which all the tetrahedral holes are filled by anions. What is the coordination number of M? of X?

7. A compound has a structure based on simple cubic packing of the anions, and the cations occupy half of the cubic holes. What is the empirical formula of this compound? What is the coordination number of the cation?

8. Barium and fluoride form a compound that crystallizes in the fluorite structure, in which the fluoride ions occupy all the tetrahedral holes in a ccp array of barium ions. This particular compound is used in embalming fluid. What is its empirical formula?

9. Cadmium chloride is used in paints as a yellow pigment. Is the following structure consistent with an empirical formula of $CdCl_2$? If not, what is the empirical formula of the structure shown?




10. Use the information in the following table to decide whether the cation will occupy a tetrahedral hole, an octahedral hole, or a cubic hole in each case.

| Cation Radius (pm) | Anion Radius (pm) |
|---|---|
| 78.0 | 132 |
| 165 | 133 |
| 81 | 174 |

11. Calculate the angle of diffraction when x-rays from a copper tube (λ = 154 pm) are diffracted by planes of atoms parallel to the faces of the cubic unit cell for Mg (260 pm), Zn (247 pm), and Ni (216 pm). The length on one edge of the unit cell is given in parentheses; assume first-order diffraction (n = 1).

12. If x-rays from a copper target (λ = 154 pm) are scattered at an angle of 17.23° by a sample of Mg, what is the distance (in picometers) between the planes responsible for this diffraction? How does this distance compare with that in a sample of Ni for which θ = 20.88°?

## Numerical Answers

3. d = 3.1805 g/cm$^3$; Avogadro's number = $6.023 \times 10^{23}$ mol$^{-1}$

5. Both have same stoichiometry, $CaTiO_3$

7. Stoichiometry is $MX_2$; coordination number of cations is 8

9. No, the structure shown has an empirical formula of $Cd_3Cl_8$.

11. Mg: 17.2°, Zn: 18.2°, Ni: 20.9°

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# 12.4: Defects in Crystals

**Learning Objectives**

- To understand the origin and nature of defects in crystals.

The crystal lattices we have described represent an idealized, simplified system that can be used to understand many of the important principles governing the behavior of solids. In contrast, real crystals contain large numbers of defects (typically more than $10^4$ per milligram), ranging from variable amounts of impurities to missing or misplaced atoms or ions. These defects occur for three main reasons:

1. It is impossible to obtain any substance in 100% pure form. Some impurities are always present.
2. Even if a substance were 100% pure, forming a perfect crystal would require cooling the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the “wrong” place in a lattice or in areas where two lattices that grew separately intersect.
3. Applying an external stress to a crystal, such as a hammer blow, can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment.

In this section, we discuss how defects determine some of the properties of solids. We begin with solids that consist of neutral atoms, specifically metals, and then turn to ionic compounds.

## Defects in Metals

Metals can have various types of defects. A point defect is any defect that involves only a single particle (a lattice point) or sometimes a very small set of points. A line defect is restricted to a row of lattice points, and a plane defect involves an entire plane of lattice points in a crystal. A vacancy occurs where an atom is missing from the normal crystalline array; it constitutes a tiny void in the middle of a solid (Figure 12.4.1). We focus primarily on point and plane defects in our discussion because they are encountered most frequently.

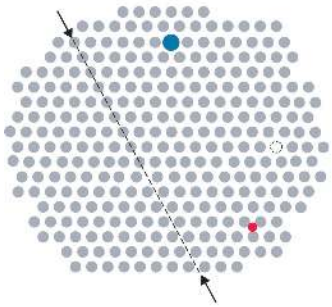


Figure 12.4.1: Common Defects in Crystals. In this two-dimensional representation of a crystal lattice containing substitutional and interstitial impurities, vacancies, and line defects, a dashed line and arrows indicate the position of the line defect.

## Impurities

Impurities can be classified as interstitial or substitutional. An interstitial impurity is usually a smaller atom (typically about 45% smaller than the host) that can fit into the octahedral or tetrahedral holes in the metal lattice (Figure 12.4.1). Steels consist of iron with carbon atoms added as interstitial impurities (Table 12.4.1). The inclusion of one or more transition metals or semimetals can improve the corrosion resistance of steel.

Table 12.4.1: Compositions, Properties, and Uses of Some Types of Steel

| Name of Steel | Typical Composition* | Properties | Applications |
|---|---|---|---|
| low-carbon | <0.15% C | soft and ductile | wire |
| mild carbon | 0.15%–0.25% C | malleable and ductile | cables, chains, and nails |
| high-carbon | 0.60%–1.5% C | hard and brittle | knives, cutting tools, drill bits, and springs |
| stainless | 15%–20% Cr, 1%–5% Mn, 5%–10% Ni, 1%–3% Si, 1% C, 0.05% P | corrosion resistant | cutlery, instruments, and marine fittings |
| invar | 36% Ni | low coefficient of thermal expansion | measuring tapes and meter sticks |
| manganese | 10%–20% Mn | hard and wear resistant | armor plate, safes, and rails |
| high-speed | 14%–20% W | retains hardness at high temperatures | high-speed cutting tools |
| silicon | 1%–5% Si | hard, strong, and highly magnetic | magnets in electric motors and transformers |

*In addition to enough iron to bring the total percentage up to 100%, most steels contain small amounts of carbon (0.5%–1.5%) and manganese (<2%).

In contrast, a substitutional impurity is a different atom of about the same size that simply replaces one of the atoms that compose the host lattice (Figure 12.4.1). Substitutional impurities are usually chemically similar to the substance that constitutes the bulk of the sample, and they generally have atomic radii that are within about 15% of the radius of the host. For example, strontium and calcium are chemically similar and have similar radii, and as a result, strontium is a common impurity in crystalline calcium, with the Sr atoms randomly occupying sites normally occupied by Ca.

> *Interstitial impurities are smaller atoms than the host atom, whereas substitutional impurities are usually chemically similar and are similar in size to the host atom.*

## Dislocations, Deformations, and Work Hardening

Inserting an extra plane of atoms into a crystal lattice produces an edge dislocation. A familiar example of an edge dislocation occurs when an ear of corn contains an extra row of kernels between the other rows (Figure 12.4.2). An edge dislocation in a crystal causes the planes of atoms in the lattice to deform where the extra plane of atoms begins (Figure 12.4.2). The edge dislocation frequently determines whether the entire solid will deform and fail under stress.

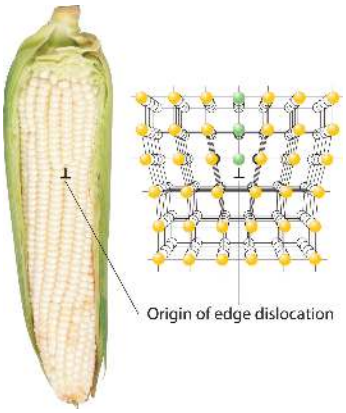



Figure 12.4.2: Edge Dislocations. *Shown are two examples of edge dislocations: (a) an edge dislocation in an ear of corn and (b) a three-dimensional representation of an edge dislocation in a solid, illustrating how an edge dislocation can be viewed as a simple line defect arising from the insertion of an extra set of atoms into the lattice. In both cases, the origin of the edge dislocation is indicated by the symbol ⊥.*

Deformation occurs when a dislocation moves through a crystal. To illustrate the process, suppose you have a heavy rug that is lying a few inches off-center on a nonskid pad. To move the rug to its proper place, you could pick up one end and pull it. Because of the large area of contact between the rug and the pad, however, they will probably move as a unit. Alternatively, you could pick up the rug and try to set it back down exactly where you want it, but that requires a great deal of effort (and probably at least one extra person). An easier solution is to create a small wrinkle at one end of the rug (an edge dislocation) and gradually push the wrinkle across, resulting in a net movement of the rug as a whole (part (a) in Figure 12.4.3). Moving the wrinkle requires only a small amount of energy because only a small part of the rug is actually moving at any one time. Similarly, in a solid, the contacts between layers are broken in only one place at a time, which facilitates the deformation process.

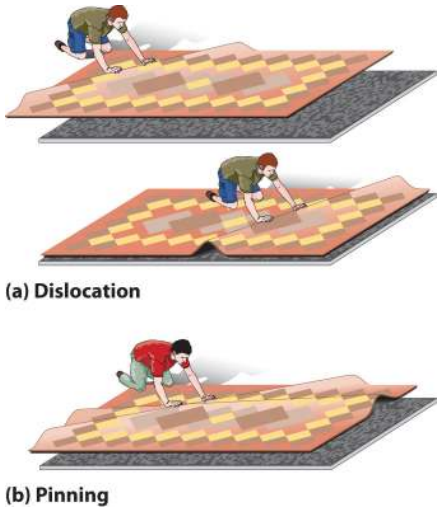



Figure 12.4.3: The Role of Dislocation in the Motion of One Planar Object across Another. (a) Pushing a wrinkle across the rug results in a net movement of the rug with relatively little expenditure of energy because at any given time only a very small amount of the rug is not in contact with the floor. (b) A second intersecting wrinkle prevents movement of the first by “pinning” it.

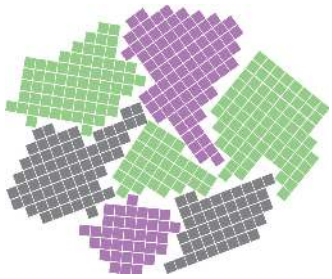
If the rug we have just described has a second wrinkle at a different angle, however, it is very difficult to move the first one where the two wrinkles intersect (part (b) in Figure 12.4.3); this process is called pinning. Similarly, intersecting dislocations in a solid prevent them from moving, thereby increasing the mechanical strength of the material. In fact, one of the major goals of materials science is to find ways to pin dislocations to strengthen or harden a material.

Pinning can also be achieved by introducing selected impurities in appropriate amounts. Substitutional impurities that are a mismatch in size to the host prevent dislocations from migrating smoothly along a plane. Generally, the higher the concentration of impurities, the more effectively they block migration, and the stronger the material. For example, bronze, which contains about 20% tin and 80% copper by mass, produces a much harder and sharper weapon than does either pure tin or pure copper. Similarly,

pure gold is too soft to make durable jewelry, so most gold jewelry contains 75% (18 carat) or 58% (14 carat) gold by mass, with the remainder consisting of copper, silver, or both.

If an interstitial impurity forms polar covalent bonds to the host atoms, the layers are prevented from sliding past one another, even when only a small amount of the impurity is present. For example, because iron forms polar covalent bonds to carbon, the strongest steels need to contain only about 1% carbon by mass to substantially increase their strength (Table 12.4.1).

Most materials are polycrystalline, which means they consist of many microscopic individual crystals called grains that are randomly oriented with respect to one another. The place where two grains intersect is called a grain boundary. The movement of a deformation through a solid tends to stop at a grain boundary. Consequently, controlling the grain size in solids is critical for obtaining desirable mechanical properties; fine-grained materials are usually much stronger than coarse-grained ones.



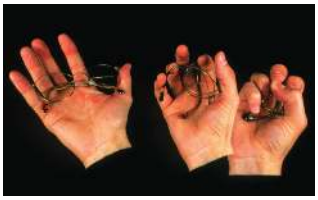
Grain boundaries. As a polycrystalline material solidifies, grains with irregular shapes form. The interfaces between grains constitute grain boundaries. (Squares represent unit cells within grains.)

Work hardening is the introduction of a dense network of dislocations throughout a solid, which makes it very tough and hard. If all the defects in a single 1 cm3 sample of a work-hardened material were laid end to end, their total length could be 106 km! The legendary blades of the Japanese and Moorish swordsmiths owed much of their strength to repeated work hardening of the steel. As the density of defects increases, however, the metal becomes more brittle (less malleable). For example, bending a paper clip back and forth several times increases its brittleness from work hardening and causes the wire to break.

## Memory Metal

The compound NiTi, popularly known as “memory metal” or nitinol (nickel–titanium Naval Ordinance Laboratory, after the site where it was first prepared), illustrates the importance of deformations. If a straight piece of NiTi wire is wound into a spiral, it will remain in the spiral shape indefinitely, unless it is warmed to 50°C–60°C, at which point it will spontaneously straighten out again. The chemistry behind the temperature-induced change in shape is moderately complex, but for our purposes it is sufficient to know that NiTi can exist in two different solid phases.

The high-temperature phase has the cubic cesium chloride structure, in which a Ti atom is embedded in the center of a cube of Ni atoms (or vice versa). The low-temperature phase has a related but kinked structure, in which one of the angles of the unit cell is no longer 90°. Bending an object made of the low-temperature (kinked) phase creates defects that change the pattern of kinks within the structure. If the object is heated to a temperature greater than about 50°C, the material undergoes a transition to the cubic high-temperature phase, causing the object to return to its original shape. The shape of the object above 50°C is controlled by a complex set of defects and dislocations that can be relaxed or changed only by the thermal motion of the atoms.



***Memory metal***. *Flexon is a fatigue-resistant alloy of Ti and Ni that is used as a frame for glasses because of its durability and corrosion resistance.*

Memory metal has many other practical applications, such as its use in temperature-sensitive springs that open and close valves in the automatic transmissions of cars. Because NiTi can also undergo pressure- or tension-induced phase transitions, it is used to

make wires for straightening teeth in orthodontic braces and in surgical staples that change shape at body temperature to hold broken bones together.

Another flexible, fatigue-resistant alloy composed of titanium and nickel is Flexon. Originally discovered by metallurgists who were creating titanium-based alloys for use in missile heat shields, Flexon is now used as a durable, corrosion-resistant frame for glasses, among other uses.

### Example 12.4.1

Because steels with at least 4% chromium are much more corrosion resistant than iron, they are collectively sold as “stainless steel.” Referring to the composition of stainless steel in Table 12.4.1 and, if needed, the atomic radii in Figure 7.7 , predict which type of impurity is represented by each element in stainless steel, excluding iron, that are present in at least 0.05% by mass.

**Given**: composition of stainless steel and atomic radii

**Asked for**: type of impurity

**Strategy**:

Using the data in Table 12.4.1 and the atomic radii in Figure 7.7, determine whether the impurities listed are similar in size to an iron atom. Then determine whether each impurity is chemically similar to Fe. If similar in both size and chemistry, the impurity is likely to be a substitutional impurity. If not, it is likely to be an interstitial impurity.

**Solution**:

According to Table 12.4.1, stainless steel typically contains about 1% carbon, 1%–5% manganese, 0.05% phosphorus, 1%–3% silicon, 5%–10% nickel, and 15%–20% chromium. The three transition elements (Mn, Ni, and Cr) lie near Fe in the periodic table, so they should be similar to Fe in chemical properties and atomic size (atomic radius = 125 pm). Hence they almost certainly will substitute for iron in the Fe lattice. Carbon is a second-period element that is nonmetallic and much smaller (atomic radius = 77 pm) than iron. Carbon will therefore tend to occupy interstitial sites in the iron lattice. Phosphorus and silicon are chemically quite different from iron (phosphorus is a nonmetal, and silicon is a semimetal), even though they are similar in size (atomic radii of 106 and 111 pm, respectively). Thus they are unlikely to be substitutional impurities in the iron lattice or fit into interstitial sites, but they could aggregate into layers that would constitute plane defects.

### Exercise 12.4.1

Consider nitrogen, vanadium, zirconium, and uranium impurities in a sample of titanium metal. Which is most likely to form an interstitial impurity? a substitutional impurity?

**Answer**: nitrogen; vanadium

## Defects in Ionic and Molecular Crystals

All the defects and impurities described for metals are seen in ionic and molecular compounds as well. Because ionic compounds contain both cations and anions rather than only neutral atoms, however, they exhibit additional types of defects that are not possible in metals.

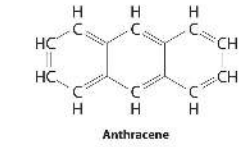
The most straightforward variant is a substitutional impurity in which a cation or an anion is replaced by another of similar charge and size. For example, $Br^-$ can substitute for $Cl^-$, so tiny amounts of $Br^-$ are usually present in a chloride salt such as $CaCl_2$ or $BaCl_2$. If the substitutional impurity and the host have different charges, however, the situation becomes more complicated. Suppose, for example, that $Sr^{2+}$ (ionic radius = 118 pm) substitutes for $K^+$ (ionic radius = 138 pm) in KCl. Because the ions are approximately the same size, $Sr^{2+}$ should fit nicely into the face-centered cubic (fcc) lattice of KCl. The difference in charge, however, must somehow be compensated for so that electrical neutrality is preserved. The simplest way is for a second $K^+$ ion to be lost elsewhere in the crystal, producing a vacancy. Thus substitution of K+ by $Sr^{2+}$ in KCl results in the introduction of two defects: a site in which an $Sr^{2+}$ ion occupies a $K^+$ position and a vacant cation site. Substitutional impurities whose charges do not match the host’s are often introduced intentionally to produce compounds with specific properties.

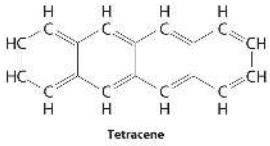
Virtually all the colored gems used in jewelry are due to substitutional impurities in simple oxide structures. For example, $\alpha$-$Al_2O_3$, a hard white solid called corundum that is used as an abrasive in fine sandpaper, is the primary component, or matrix, of a wide variety of gems. Because many trivalent transition metal ions have ionic radii only a little larger than the radius of $Al^{3+}$ (ionic radius = 53.5 pm), they can replace $Al^{3+}$ in the octahedral holes of the oxide lattice. Substituting small amounts of Cr3+ ions (ionic radius = 75 pm) for $Al^{3+}$ gives the deep red color of ruby, and a mixture of impurities ($Fe^{2+}$, $Fe^{3+}$, and $Ti^{4+}$) gives the deep blue of sapphire. True amethyst contains small amounts of $Fe^{3+}$ in an $SiO_2$ (quartz) matrix. The same metal ion substituted into different mineral lattices can produce very different colors. For example, $Fe^{3+}$ ions are responsible for the yellow color of topaz and the violet color of amethyst. The distinct environments cause differences in d orbital energies, enabling the $Fe^{3+}$ ions to absorb light of different frequencies, a topic discussed later.




The same cation in different environments. An $Fe^{3+}$ substitutional impurity produces substances with strikingly different colors.

Substitutional impurities are also observed in molecular crystals if the structure of the impurity is similar to the host, and they can have major effects on the properties of the crystal. Pure anthracene, for example, is an electrical conductor, but the transfer of electrons through the molecule is much slower if the anthracene crystal contains even very small amounts of tetracene despite their strong structural similarities.




If a cation or an anion is simply missing, leaving a vacant site in an ionic crystal, then for the crystal to be electrically neutral, there must be a corresponding vacancy of the ion with the opposite charge somewhere in the crystal. In compounds such as KCl, the charges are equal but opposite, so one anion vacancy is sufficient to compensate for each cation vacancy. In compounds such as $CaCl_2$, however, two $Cl^-$ anion sites must be vacant to compensate for each missing $Ca^{2+}$ cation. These pairs (or sets) of vacancies are called Schottky defects and are particularly common in simple alkali metal halides such as KCl (part (a) in Figure 12.4.4). Many microwave diodes, which are devices that allow a current to flow in a single direction, are composed of materials with Schottky defects.

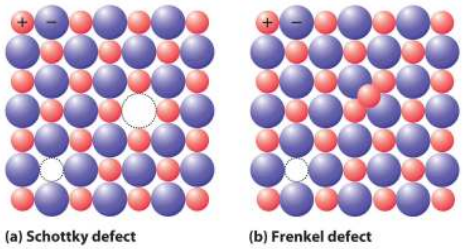



Figure 12.4.4: The Two Most Common Defects in Ionic Solids. (a) A Schottky defect in KCl shows the missing cation/anion pair. (b) A Frenkel defect in AgI shows a misplaced $Ag^+$ cation.

Occasionally one of the ions in an ionic lattice is simply in the wrong position. An example of this phenomenon, called a Frenkel defect, is a cation that occupies a tetrahedral hole rather than an octahedral hole in the anion lattice (part (b) in Figure 12.4.4). Frenkel defects are most common in salts that have a large anion and a relatively small cation. To preserve electrical neutrality, one of the normal cation sites, usually octahedral, must be vacant.

Frenkel defects are particularly common in the silver halides AgCl, AgBr, and AgI, which combine a rather small cation ($Ag^+$, ionic radius = 115 pm) with large, polarizable anions. Certain more complex salts with a second cation in addition to $Ag^+$ and $Br^−$ or $I^−$ have so many Ag+ ions in tetrahedral holes that they are good electrical conductors in the solid state; hence they are called solid electrolytes. Since most ionic compounds do not conduct electricity in the solid state, however they do conduct electricity when molten or dissolved in a solvent that separates the ions, allowing them to migrate in response to an applied electric field.) In response to an applied voltage, the cations in solid electrolytes can diffuse rapidly through the lattice via octahedral holes, creating Frenkel defects as the cations migrate. Sodium–sulfur batteries use a solid $Al_2O_3$ electrolyte with small amounts of solid $Na_2O$. Because the electrolyte cannot leak, it cannot cause corrosion, which gives a battery that uses a solid electrolyte a significant advantage over one with a liquid electrolyte.

### ✔ Example 12.4.2

In a sample of NaCl, one of every 10,000 sites normally occupied by $Na^+$ is occupied instead by $Ca^{2+}$. Assuming that all of the $Cl^−$ sites are fully occupied, what is the stoichiometry of the sample?

**Given**: ionic solid and number and type of defect

**Asked for**: stoichiometry

**Strategy**:

A. Identify the unit cell of the host compound. Compute the stoichiometry if 0.01% of the $Na^+$ sites are occupied by $Ca^{2+}$. If the overall charge is greater than 0, then the stoichiometry must be incorrect.
B. If incorrect, adjust the stoichiometry of the $Na^+$ ion to compensate for the additional charge.

**Solution**:

**A** Pure NaCl has a 1:1 ratio of $Na^+$ and $Cl^−$ ions arranged in an fcc lattice (the sodium chloride structure). If all the anion sites are occupied by $Cl^−$, the negative charge is −1.00 per formula unit. If 0.01% of the $Na^+$ sites are occupied by $Ca^{2+}$ ions, the cation stoichiometry is Na0.99Ca0.01. This results in a positive charge of (0.99)(+1) + (0.01)(+2) = +1.01 per formula unit, for a net charge in the crystal of +1.01 + (−1.00) = +0.01 per formula unit. Because the overall charge is greater than 0, this stoichiometry must be incorrect.

**B** The most plausible way for the solid to adjust its composition to become electrically neutral is for some of the $Na^+$ sites to be vacant. If one $Na^+$ site is vacant for each site that has a $Ca^{2+}$ cation, then the cation stoichiometry is Na0.98Ca0.01. This results in a positive charge of (0.98)(+1) + (0.01)(+2) = +1.00 per formula unit, which exactly neutralizes the negative charge. The stoichiometry of the solid is thus $Na_{0.98}Ca_{0.01}Cl_{1.00}$.

### ? Exercise 12.4.2

In a sample of MgO that has the sodium chloride structure, 0.02% of the $Mg^{2+}$ ions are replaced by $Na^+$ ions. Assuming that all of the cation sites are fully occupied, what is the stoichiometry of the sample?

**Answer**: If the formula of the compound is $Mg_{0.98}Na_{0.02}O_{1−x}$, then x must equal 0.01 to preserve electrical neutrality. The formula is thus $Mg_{0.98}Na_{0.02}O_{0.99}$.

## Nonstoichiometric Compounds

The law of multiple proportions, states that chemical compounds contain fixed integral ratios of atoms. In fact, nonstoichiometric compounds contain large numbers of defects, usually vacancies, which give rise to stoichiometries that can depart significantly from simple integral ratios without affecting the fundamental structure of the crystal. Nonstoichiometric compounds frequently consist of transition metals, lanthanides, and actinides, with polarizable anions such as oxide ($O^{2−}$) and sulfide ($S^{2−}$). Some

common examples are listed in Table 12.4.2, along with their basic structure type. These compounds are nonstoichiometric because their constituent metals can exist in multiple oxidation states in the solid, which in combination preserve electrical neutrality.

Table 12.4.2: Some Nonstoichiometric Compounds

| Compound | Observed Range of x |
|---|---|
| **Oxides*** | |
| $Fe_xO$ | 0.85–0.95 |
| $Ni_xO$ | 0.97–1.00 |
| $TiO_x$ | 0.75–1.45 |
| $VO_x$ | 0.9–1.20 |
| $NbO_x$ | 0.9–1.04 |
| **Sulfides** | |
| $Cu_xS$ | 1.77–2.0 |
| $Fe_xS$ | 0.80–0.99 |
| $ZrS_x$ | 0.9–1.0 |

*All the oxides listed have the sodium chloride structure.

One example is iron(II) oxide (ferrous oxide), which produces the black color in clays and is used as an abrasive. Its stoichiometry is not FeO because it always contains less than 1.00 Fe per $O^{2-}$ (typically 0.90–0.95). This is possible because Fe can exist in both the +2 and +3 oxidation states. Thus the difference in charge created by a vacant $Fe^{2+}$ site can be balanced by two $Fe^{2+}$ sites that have $Fe^{3+}$ ions instead [+2 vacancy = (3 − 2) + (3 − 2)]. The crystal lattice is able to accommodate this relatively high fraction of substitutions and vacancies with no significant change in structure.

> *Because a crystal must be electrically neutral, any defect that affects the number or charge of the cations must be compensated by a corresponding defect in the number or charge of the anions.*

## Summary

Real crystals contain large numbers of defects. Defects may affect only a single point in the lattice (a point defect), a row of lattice points (a line defect), or a plane of atoms (a plane defect). A point defect can be an atom missing from a site in the crystal (a vacancy) or an impurity atom that occupies either a normal lattice site (a substitutional impurity) or a hole in the lattice between atoms (an interstitial impurity). In an edge dislocation, an extra plane of atoms is inserted into part of the crystal lattice. Multiple defects can be introduced into materials so that the presence of one defect prevents the motion of another, in a process called pinning. Because defect motion tends to stop at grain boundaries, controlling the size of the grains in a material controls its mechanical properties. In addition, a process called work hardening introduces defects to toughen metals. Schottky defects are a coupled pair of vacancies—one cation and one anion—that maintains electrical neutrality. A Frenkel defect is an ion that occupies an incorrect site in the lattice. Cations in such compounds are often able to move rapidly from one site in the crystal to another, resulting in high electrical conductivity in the solid material. Such compounds are called solid electrolytes. Nonstoichiometric compounds have variable stoichiometries over a given range with no dramatic change in crystal structure. This behavior is due to a large number of vacancies or substitutions of one ion by another ion with a different charge.

## Conceptual Problems

1. How are defects and impurities in a solid related? Can a pure, crystalline compound be free of defects? How can a substitutional impurity produce a vacancy?

2. Why does applying a mechanical stress to a covalent solid cause it to fracture? Use an atomic level description to explain why a metal is ductile under conditions that cause a covalent solid to fracture.

3. How does work hardening increase the strength of a metal? How does work hardening affect the physical properties of a metal?

4. Work-hardened metals and covalent solids such as diamonds are both susceptible to cracking when stressed. Explain how such different materials can both exhibit this property.

5. Suppose you want to produce a ductile material with improved properties. Would impurity atoms of similar or dissimilar atomic size be better at maintaining the ductility of a metal? Why? How would introducing an impurity that forms polar covalent bonds with the metal atoms affect the ductility of the metal? Explain your reasoning.

6. Substitutional impurities are often used to tune the properties of material. Why are substitutional impurities generally more effective at high concentrations, whereas interstitial impurities are usually effective at low concentrations?

7. If an $O^{2-}$ ion (ionic radius = 132 pm) is substituted for an $F^-$ ion (ionic radius = 133 pm) in an ionic crystal, what structural changes in the ionic lattice will result?

8. How will the introduction of a metal ion with a different charge as an impurity induce the formation of oxygen vacancies in an ionic metal-oxide crystal?

9. Many nonstoichiometric compounds are transition metal compounds. How can such compounds exist, given that their nonintegral cation:anion ratios apparently contradict one of the basic tenets of Dalton's atomic theory of matter?

10. If you wanted to induce the formation of oxygen vacancies in an ionic crystal, which would you introduce as substitutional impurities—cations with a higher positive charge or a lower positive charge than the cations in the parent structure? Explain your reasoning.

## Conceptual Answers

5. Impurity atoms of similar size and with similar chemical properties would be most likely to maintain the ductility of the metal, because they are unlikely to have a large effect on the ease with which one layer of atoms can move past another under mechanical stress. Larger impurity atoms are likely to form "bumps" or kinks that will make it harder for layers of atoms to move across one another. Interstitial atoms that form polar covalent bonds with the metal atoms tend to occupy spaces between the layers; they act as a "glue" that holds layers of metal atoms together, which greatly decreases the ductility.

7. Since $O^{2-}$ and $F^-$ are both very similar in size, substitution is possible without disruption of the ionic packing. The difference in charge, however, requires the formation of a vacancy on another $F^-$ site to maintain charge neutrality.

9. Most transition metals form at least two cations that differ by only one electron. Consequently, nonstoichiometric compounds containing transition metals can maintain electrical neutrality by gaining electrons to compensate for the absence of anions or the presence of additional metal ions. Conversely, such compounds can lose electrons to compensate for the presence of additional anions or the absence of metal ions. In both cases, the positive charge on the transition metal is adjusted to maintain electrical neutrality.

## Numerical Problems

1. The ionic radius of $K^+$ is 133 pm, whereas that of $Na^+$ is 98 pm. Do you expect $K^+$ to be a common substitutional impurity in compounds containing $Na^+$? Why or why not?

2. Given Cs (262 pm), Tl (171 pm), and B (88 pm) with their noted atomic radii, which atom is most likely to act as an interstitial impurity in an Sn lattice (Sn atomic radius = 141 pm)? Why?

3. After aluminum, iron is the second most abundant metal in Earth's crust. The silvery-white, ductile metal has a body-centered cubic (bcc) unit cell with an edge length of 286.65 pm.

   a. Use this information to calculate the density of iron.

   b. What would the density of iron be if 0.15% of the iron sites were vacant?

   c. How does the mass of 1.00 $cm^3$ of iron without defects compare with the mass of 1.00 $cm^3$ of iron with 0.15% vacancies?

4. Certain ceramic materials are good electrical conductors due to high mobility of oxide ions resulting from the presence of oxygen vacancies. Zirconia ($ZrO_2$) can be doped with yttrium by adding $Y_2O_3$. If 0.35 g of $Y_2O_3$ can be incorporated into 25.0 g of $ZrO_2$ while maintaining the zirconia structure, what is the percentage of oxygen vacancies in the structure?

5. Which of the following ions is most effective at inducing an $O^{2-}$ vacancy in crystal of CaO? The ionic radii are $O^{2-}$, 132 pm; $Ca^{2+}$, 100 pm; $Sr^{2+}$, 127 pm; $F^-$, 133 pm; $La^{3+}$, 104 pm; and $K^+$, 133 pm. Explain your reasoning.

## Numerical Answers

1. No. The potassium is much larger than the sodium ion.

3.

a. 7.8744 g/cm$^3$

b. 7.86 g/cm$^3$

c. Without defects, the mass is 0.15% greater.

5. The lower charge of $K^+$ makes it the best candidate for inducing an oxide vacancy, even though its ionic radius is substantially larger than that of $Ca^{2+}$. Substituting two $K^+$ ions for two $Ca^{2+}$ ions will decrease the total positive charge by two, and an oxide vacancy will maintain electrical neutrality. For example, if 10% of the $Ca^{2+}$ ions are replaced by $K^+$, we can represent the change as going from $Ca_{20}O_{20}$ to $K_2Ca_{18}O_{20}$, which has a net charge of +2. Loss of one oxide ion would give a composition of $K_2Ca_{18}O_{19}$, which is electrically neutral.

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# 12.5: Bonding and Properties of Solids

**Learning Objectives**

- To understand the correlation between bonding and the properties of solids.

Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as *ionic*, *molecular*, *covalent* (*network*), or *metallic*. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

## Ionic Solids

You learned in Chapter 4 that an ionic solidA solid that consists of positively and negatively charged ions held together by electrostatic forces. consists of positively and negatively charged ions held together by electrostatic forces. (For more information about ionic solids, see Section 4.2.) The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy**, the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase, is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: $Na^+$ (102 pm) versus $Ca^{2+}$ (100 pm), and $F^-$ (133 pm) versus $O^{2-}$ (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

## Molecular Solids

Molecular solidsA solid that consists of molecules held together by relatively weak forces, such as dipole-dipole interactions, hydrogen bonds, and London dispersion forces. consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these, which were discussed in Chapter 11. The arrangement of the molecules in solid benzene is as follows:



**The structure of solid benzene.** In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles.

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized ($\Delta H_{fus}$ and $\Delta H_{vap}$ are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene ($C_6H_6$), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol)

< anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and *m*-xylene [$m$-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



**Toluene and *m*-xylene.** The methyl groups attached to the phenyl ring in toluene and *m*-xylene prevent the rings from packing together as in solid benzene.

## Covalent Solids

Covalent solidsA solid that consists of two- or three-dimensional networks of atoms held together by covalent bonds. are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 12.5.1, consists of $sp^3$ hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.



Figure 12.5.1The Structures of Diamond and Graphite (a) Diamond consists of $sp^3$ hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz ($SiO_2$), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure 12.5.1. It contains planar networks of six-membered rings of $sp^2$ hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized $2p_z$ orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 5 . In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent

with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons.

Table 12.5.1 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

**Table 12.5.1 A Comparison of Intermolecular ($\Delta H_{sub}$) and Intramolecular Interactions**

| Substance | $\Delta H_{sub}$ (kJ/mol) | Average Bond Energy (kJ/mol) |
|---|---|---|
| phosphorus (s) | 58.98 | 201 |
| sulfur (s) | 64.22 | 226 |
| iodine (s) | 62.42 | 149 |

## Metallic Solids

Metals are characterized by their ability to reflect light, called lusterThe ability to reflect light. Metals, for instance, have a shiny surface that reflects light (metals are lustrous), whereas nonmetals do not., their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solidsA solid that consists of metal atoms held together by metallic bonds. are dense, with each atom having as many as 12 nearest neighbors.

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

### Note the Pattern

Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the *d* block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron seaValence electrons that are delocalized throughout a metallic solid. (Figure 12.5.2). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other

properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. A more complete description of metallic bonding is presented in Section 12.6.



Figure 12.5.2 The Electron-Sea Model of Bonding in Metals Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

## Substitutional Alloys

An alloyA solid solution of two or more metals whose properties differ from those of the constituent elements. is a mixture of metals with metallic properties that differ from those of its constituent elements. Brass (Cu and Zn in a 2:1 ratio) and bronze (Cu and Sn in a 4:1 ratio) are examples of substitutional alloysAn alloy formed by the substitution of one metal atom for another of similar size in the lattice., which are metallic solids with large numbers of substitutional impurities. In contrast, small numbers of interstitial impurities, such as carbon in the iron lattice of steel, give an interstitial alloyAn alloy formed by inserting smaller atoms into holes in the metal lattice.. Because scientists can combine two or more metals in varying proportions to tailor the properties of a material for particular applications, most of the metallic substances we encounter are actually alloys. Examples include the low-melting-point alloys used in solder (Pb and Sn in a 2:1 ratio) and in fuses and fire sprinklers (Bi, Pb, Sn, and Cd in a 4:2:1:1 ratio).

The compositions of most alloys can vary over wide ranges. In contrast, intermetallic compoundsAn alloy that consists of certain metals that combine in only specific proportions and whose properties are frequently quite different from those of their constituent elements. consist of certain metals that combine in only specific proportions. Their compositions are largely determined by the relative sizes of their component atoms and the ratio of the total number of valence electrons to the number of atoms present (the *valence electron density*). The structures and physical properties of intermetallic compounds are frequently quite different from those of their constituent elements, but they may be similar to elements with a similar valence electron density. For example, $Cr_3Pt$ is an intermetallic compound used to coat razor blades advertised as "platinum coated"; it is very hard and dramatically lengthens the useful life of the razor blade. With similar valence electron densities, Cu and PdZn have been found to be virtually identical in their catalytic properties.

Some general properties of the four major classes of solids are summarized in Table 12.5.2.

**Table 12.5.2Properties of the Major Classes of Solids**

| Ionic Solids | Molecular Solids | Covalent Solids | Metallic Solids |
|---|---|---|---|
| poor conductors of heat and electricity | poor conductors of heat and electricity | poor conductors of heat and electricity* | good conductors of heat and electricity |
| relatively high melting point | low melting point | high melting point | melting points depend strongly on electron configuration |
| hard but brittle; shatter under stress | soft | very hard and brittle | easily deformed under stress; ductile and malleable |
| relatively dense | low density | low density | usually high density |
| dull surface | dull surface | dull surface | lustrous |

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

### Note the Pattern

The general order of increasing strength of interactions in a solid is molecular solids < ionic solids ≈ metallic solids < covalent solids.

### Example 12.5.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

**Given:** compounds

**Asked for:** classification and order of melting points

**Strategy:**

**A** Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.

**B** Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

**Solution:**

**A** Germanium lies in the *p* block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing $Rb^+$ and $I^-$ ions. The compound $C_6(CH_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a *d*-block element, so it is a metallic solid.

**B** Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

Exercise

Classify $C_{60}$, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

**Answer:** $C_{60}$ (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are $C_{60}$, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

### Summary

The major types of solids are ionic, molecular, covalent, and metallic. **Ionic solids** consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. **Molecular solids** are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. **Covalent solids** consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. **Metallic solids** have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An **alloy** is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (**substitutional alloys**), by inserting smaller atoms into holes in the metal lattice (**interstitial alloys**), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form **intermetallic compounds** with unique properties.

### Key Takeaway

- Solids can be classified as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions is molecular < ionic ≈ metallic < covalent.

## Conceptual Problems

1. Four vials labeled A–D contain sucrose, zinc, quartz, and sodium chloride, although not necessarily in that order. The following table summarizes the results of the series of analyses you have performed on the contents:

| | A | B | C | D |
|---|---|---|---|---|
| Melting Point | high | high | high | low |
| Thermal Conductivity | poor | poor | good | poor |
| Electrical Conductivity in Solid State | moderate | poor | high | poor |
| Electrical Conductivity in Liquid State | high | poor | high | poor |
| Hardness | hard | hard | soft | soft |
| Luster | none | none | high | none |

   Match each vial with its contents.

2. Do ionic solids generally have higher or lower melting points than molecular solids? Why? Do ionic solids generally have higher or lower melting points than covalent solids? Explain your reasoning.
3. The strength of London dispersion forces in molecular solids tends to increase with molecular mass, causing a smooth increase in melting points. Some molecular solids, however, have significantly lower melting points than predicted by their molecular masses. Why?
4. Suppose you want to synthesize a solid that is both heat resistant and a good electrical conductor. What specific types of bonding and molecular interactions would you want in your starting materials?
5. Explain the differences between an interstitial alloy and a substitutional alloy. Given an alloy in which the identity of one metallic element is known, how could you determine whether it is a substitutional alloy or an interstitial alloy?
6. How are intermetallic compounds different from interstitial alloys or substitutional alloys?

## Answers

1. 1. NaCl, ionic solid
   2. quartz, covalent solid
   3. zinc, metal
   4. sucrose, molecular solid
2. 
3. 
4. 
5. In a substitutional alloy, the impurity atoms are similar in size and chemical properties to the atoms of the host lattice; consequently, they simply replace some of the metal atoms in the normal lattice and do not greatly perturb the structure and physical properties. In an interstitial alloy, the impurity atoms are generally much smaller, have very different chemical properties, and occupy holes between the larger metal atoms. Because interstitial impurities form covalent bonds to the metal atoms in the host lattice, they tend to have a large effect on the mechanical properties of the metal, making it harder, less ductile, and more brittle. Comparing the mechanical properties of an alloy with those of the parent metal could be used to decide whether the alloy were a substitutional or interstitial alloy.
6. 

## Numerical Problems

1. Will the melting point of lanthanum(III) oxide be higher or lower than that of ferrous bromide? The relevant ionic radii are as follows: $La^{3+}$, 104 pm; $O^{2-}$, 132 pm; $Fe^{2+}$, 83 pm; and $Br^{-}$, 196 pm. Explain your reasoning.
2. Draw a graph showing the relationship between the electrical conductivity of metallic silver and temperature.
3. Which has the higher melting point? Explain your reasoning in each case.
    1. Os or Hf
    2. $SnO_2$ or $ZrO_2$
    3. $Al_2O_3$ or $SiO_2$
4. Draw a graph showing the relationship between the electrical conductivity of a typical semiconductor and temperature.

## Answer

1. 
2. 
3. 
    1. Osmium has a higher melting point, due to more valence electrons for metallic bonding.
    2. Zirconium oxide has a higher melting point, because it has greater ionic character.
    3. Aluminum oxide has a higher melting point, again because it has greater ionic character.
4. 

## Contributors

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# 12.6: Metals and Semiconductors

**Learning Objectives**

- To describe the electrical properties of a solid using band theory.

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model described in Section 12.5 . The molecular orbital theory we used in Section 6.5 to explain the delocalized π bonding in polyatomic ions and molecules such as $NO_2^-$, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

## Band Theory

In a 1 mol sample of a metal, there can be more than $10^{24}$ orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of *n* metal atoms, each containing a single electron in an *s* orbital. We use this example to describe an approach to metallic bonding called band theoryA theory used to describe the bonding in metals and semiconductors., which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

## One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure 12.6.1 shows the pattern of molecular orbitals that results from the interaction of *ns* orbitals as *n* increases from 2 to 5.

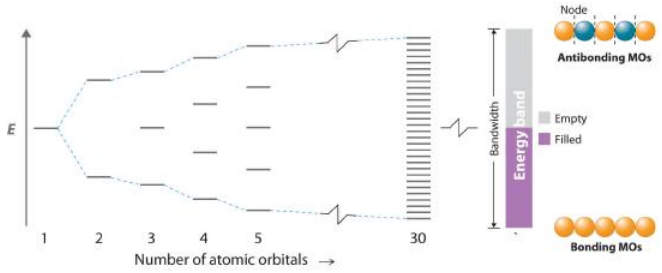



Figure 12.6.1 The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of *n* Atoms, Each of Which Contains a Singly Occupied *s* Orbital The far right-hand portion, corresponding to $n = 30$ and $n = \infty$. As *n* becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.

As we saw in Chapter 6, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For $n = 30$, there are still discrete, well-resolved energy levels, but as *n* increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure 12.6.1, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure 12.6.1 is called an energy bandThe continuous set of allowed energy levels generated in band theory when the valence orbitals of the atoms in a solid interact with one another, thus creating a set of molecular orbitals that extend throughout the solid.. The difference in energy between the highest and lowest energy levels is the bandwidthThe difference in energy between the highest and lowest energy levels in an energy band. and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the

same as the number of interacting atomic orbitals, the band in Figure 12.6.1 contains *n* energy levels corresponding to the combining of *s* orbitals from *n* metal atoms. Each of the original *s* orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2*n* electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each *s* orbital, so there are only *n* electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the *bonding* molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

## Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only *s* orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in *p* and *d* orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 12.6.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

## Band Gap

Because the 1*s*, 2*s*, and 2*p* orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 12.6.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gapThe difference in energy between the highest level of one energy band and the lowest level of the band above it, which represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

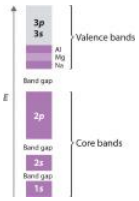



Figure 12.6.2 The Band Structures of the Period 3 Metals Na, Mg, and Al The 3*s* and 3*p* valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3*s* and 3*p* in Figure 12.6.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3*s* and 3*p* atomic orbitals are wider than the energy gap between them, so the result is overlapping bandsMolecular orbitals derived from two or more different kinds of valence electrons that have similar energies.. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3*s* and 3*p* bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3*s* orbital and six electrons for each set of 3*p* orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 12.6.2. The partially filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When

the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

## Requirements for Metallic Behavior

For a solid to exhibit metallic behavior, it must have a set of delocalized orbitals forming a band of allowed energy levels, and the resulting band must be only partially filled (10%–90%) with electrons. Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

### Note the Pattern

Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence *ns*, (*n* − 1)*d*, and *np* orbitals (with a total capacity of 18 electrons per metal atom) or their *ns* and (*n* − 1)*d* orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

## Insulators

In contrast to metals, electrical insulatorsA material that conducts electricity poorly because its valence bands are full. are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in part (a) in Figure 12.6.3. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2*s* and 2*p* orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

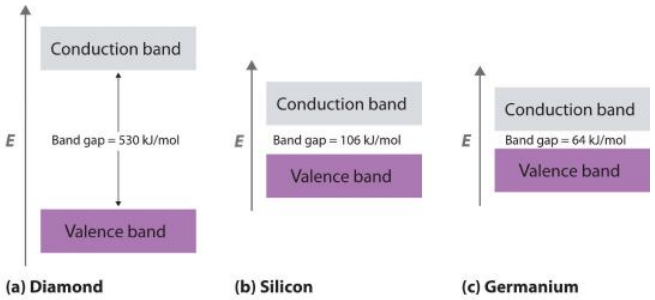



Figure 12.6.3 Energy-Band Diagrams for Diamond, Silicon, and Germanium The band gap gets smaller from C to Ge.

## Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure 12.6.3"). (For more information on bond strengths, see Section 5.5.) Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction bandThe band of empty molecular orbitals in a semiconductor..

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a *positive* charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure 12.6.4). Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductorsA substance such as Si and Ge that has a conductivity between that of metals and insulators.. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure 12.6.5.

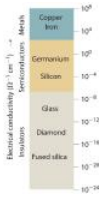



**Figure 12.6.4** A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

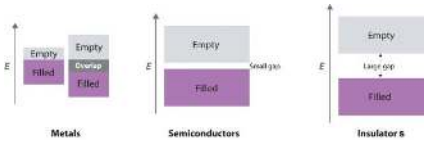



Figure 12.6.5A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and InsulatorsMetallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

## Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the *net* motion of the electron through the crystal, and the *lower* the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus *decreasing* the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 12.6.6.

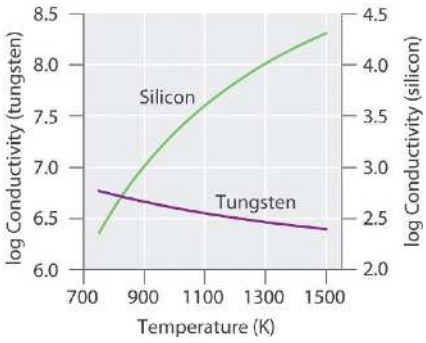



Figure 12.6.6 The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

### Note the Pattern

The electrical conductivity of a semiconductor *increases* with increasing temperature, whereas the electrical conductivity of a metal *decreases* with increasing temperature.

## *n*- and *p*-Type Semiconductors

DopingThe process of deliberately introducing small amounts of impurities into commercial semiconductors to tune their electrical properties for specific applications. is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains *more* valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in part (a) in Figure 12.6.7, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an *n*-type semiconductorA semiconductor that has been doped with an impurity that has more valence electrons than the atoms of the host lattice., with the *n* indicating that the added charge carriers are negative (they are electrons).

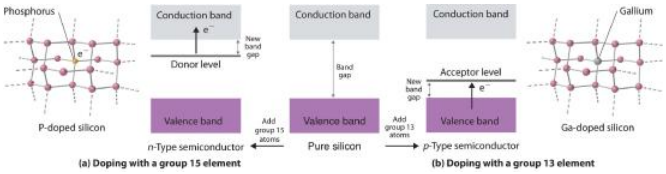



Figure 12.6.7 Structures and Band Diagrams of *n*-Type and *p*-Type Semiconductors (a) Doping silicon with a group 15 element results in a new *filled* level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new *empty* level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.

If the impurity atoms contain *fewer* valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in *increased* conductivity because the impurity atoms generate holes in the valence band. As shown in part (b) in Figure 12.27, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p*-type semiconductorA semiconductor that has been doped with an impurity that has fewer valence electrons than the atoms of the host lattice., with the *p* standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

### Note the Pattern

*n*-Type semiconductors are *n*egative charge carriers; the impurity has *more* valence electrons than the host. *p*-Type semiconductors are *p*ositive charge carriers; the impurity has *fewer* valence electrons than the host.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between *n*- and *p*-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced *p*-type semiconductors, whereas doping them with boron and deuterium achieves *n*-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

### Example 12.6.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.




1. Predict the electrical properties of this solid.
2. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
3. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

**Given:** band structure

**Asked for:** variations in electrical properties with conditions

**Strategy:**

**A** Based on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.

**B** After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.

**C** Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

**Solution:**

1. **A** The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
2. **B** Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.

3. **C** Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



1. Predict the electrical properties of the solid.
2. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
3. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

**Answer**

1. The solid has a partially filled band, so it has the electrical properties of a conductor.
2. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
3. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

## Summary

**Band theory** assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an **energy band**. The difference in energy between the highest and lowest allowed levels within a given band is the **bandwidth**, and the difference in energy between the highest level of one band and the lowest level of the band above it is the **band gap**. If the width of adjacent bands is larger than the energy gap between them, **overlapping bands** result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a **conduction band**), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. **Electrical insulators** are poor conductors because their valence bands are full. **Semiconductors** have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by **doping**, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an ***n*-type semiconductor** with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a ***p*-type semiconductor** that also exhibits increased electrical conductivity.

## Key Takeaway

- Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid.

## Conceptual Problems

1. Can band theory be applied to metals with two electrons in their valence *s* orbitals? with no electrons in their valence *s* orbitals? Why or why not?
2. Given a sample of a metal with $10^{20}$ atoms, how does the width of the band arising from *p* orbital interactions compare with the width of the band arising from *s* orbital interactions? from *d* orbital interactions?
3. Diamond has one of the lowest electrical conductivities known. Based on this fact, do you expect diamond to be colored? Why? How do you account for the fact that some diamonds are colored (such as “pink” diamond or “green” diamond)?

4. Why do silver halides, used in the photographic industry, have band gaps typical of semiconducting materials, whereas alkali metal halides have very large band gaps?
5. As the ionic character of a compound increases, does its band gap increase or decrease? Why?
6. Why is silicon, rather than carbon or germanium, used in the semiconductor industry?
7. Carbon is an insulator, and silicon and germanium are semiconductors. Explain the relationship between the valence electron configuration of each element and their band structures. Which will have the higher electrical conductivity at room temperature—silicon or germanium?
8. How does doping affect the electrical conductivity of a semiconductor? Draw the effect of doping on the energy levels of the valence band and the conduction band for both an *n*-type and a *p*-type semiconductor.

## Answers

1.
2.
3. The low electrical conductivity of diamond implies a very large band gap, corresponding to the energy of a photon of ultraviolet light rather than visible light. Consequently, diamond should be colorless. Pink or green diamonds contain small amounts of highly colored impurities that are responsible for their color.
4.
5. As the ionic character of a compound increases, the band gap will also increase due to a decrease in orbital overlap. Remember that overlap is greatest for orbitals of the same energy, and that the difference in energy between orbitals on adjacent atoms increases as the difference in electronegativity between the atoms increases. Thus, large differences in electronegativity increase the ionic character, decrease the orbital overlap, and increase the band gap.
6.
7.
8.

## Numerical Problems

1. Of Ca, N, B, and Ge, which will convert pure silicon into a *p*-type semiconductor when doping? Explain your reasoning.
2. Of Ga, Si, Br, and P, which will convert pure germanium into an *n*-type semiconductor when doping? Explain your reasoning.

## Contributors

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# 12.7: Superconductors

**Learning Objectives**

- To become familiar with the properties of superconductors.

The phenomenon of superconductivity was discovered by the Danish physicist H. Kamerlingh Onnes (1853–1926; Nobel Prize in Physics, 1913), who found a way to liquefy helium, which boils at 4.2 K and 1 atm pressure. To exploit the very low temperatures made possible by this new cryogenic fluid, he began a systematic study of the properties of metals, especially their electrical properties. Because the electrical resistance of a sample is technically easier to measure than its conductivity, Onnes measured the *resistivity* of his samples. The resistivity and conductivity of a material are inversely proportional:

$$conductivity = \frac{1}{resistivity} \tag{12.7.1}$$

In 1911, Onnes discovered that at about 4 K, the resistivity of metallic mercury (melting point = 234 K) decreased suddenly to essentially zero, rather than continuing to decrease only slowly with decreasing temperature as expected (Figure 12.7.1). He called this phenomenon superconductivityThe phenomenon in which a solid at low temperatures exhibits zero resistance to the flow of electrical current. because a resistivity of zero means that an electrical current can flow forever. Onnes soon discovered that many other metallic elements exhibit superconductivity at very low temperatures. Each of these superconductorsA solid that at low temperatures exhibits zero resistance to the flow of electrical current. has a characteristic superconducting transition temperature ($T_c$)The temperature at which the electrical resistance of a material drops to zero. at which its resistivity drops to zero. At temperatures less than their $T_c$, superconductors also completely expel a magnetic field from their interior (part (a) in Figure 12.7.2 ). This phenomenon is called the Meissner effectThe phenomenon in which a superconductor completely expels a magnetic field from its interior. after one of its discoverers, the German physicist Walther Meissner, who described the phenomenon in 1933. Due to the Meissner effect, a superconductor will actually “float” over a magnet, as shown in part (b) in Figure 12.7.2.

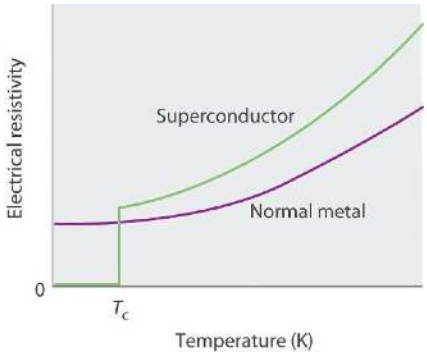
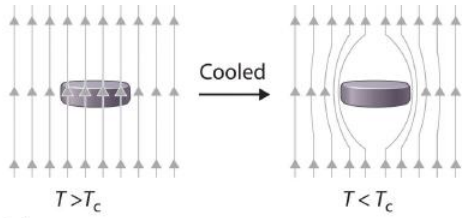



Figure 12.7.1The Temperature Dependence of the Electrical Resistivity of a Normal Metal and a Superconductor The superconducting transition temperature ($T_c$) is the temperature at which the resistivity of a superconductor drops to zero.




(a)



(b)

Figure 12.7.2 The Meissner Effect (a) Below its $T_c$, a superconductor completely expels magnetic lines of force from its interior. (b) In magnetic levitation, a small magnet "floats" over a disk of a high-temperature superconducting material ($YBa_2Cu_3O_{7-x}$) cooled in liquid nitrogen.

## BCS Theory

For many years, the phenomenon of superconductivity could not be satisfactorily explained by the laws of conventional physics. In the early 1950s, however, American physicists John Bardeen, Leon Cooper, and John Schrieffer formulated a theory for superconductivity that earned them the Nobel Prize in Physics in 1972. According to the BCS theoryA theory used to explain the phenomenon of superconductivity. (named for the initials of their last names), electrons are able to travel through a solid with zero resistance because of attractive interactions involving two electrons that are at some distance from each other. As one electron moves through the lattice, the surrounding nuclei are attracted to it. The motion of the nuclei can create a transient (short-lived) hole that pulls the second electron in the same direction as the first. The nuclei then return to their original positions to avoid colliding with the second electron as it approaches. The pairs of electrons, called Cooper pairsPairs of electrons that migrate through a superconducting material as a unit., migrate through the crystal as a unit. The electrons in Cooper pairs change partners frequently, like dancers in a ballet.

According to the BCS theory, as the temperature of the solid increases, the vibrations of the atoms in the lattice increase continuously, until eventually the electrons cannot avoid colliding with them. The collisions result in the loss of superconductivity at higher temperatures.

The phenomenon of superconductivity suggested many exciting technological applications. For example, using superconducting wires in power cables would result in zero power losses, even over distances of hundreds of miles. Additionally, because superconductors expel magnetic fields, a combination of magnetic rails and superconducting wheels (or vice versa) could be used to produce *magnetic levitation* of, for example, a train over the track, resulting in friction-free transportation.

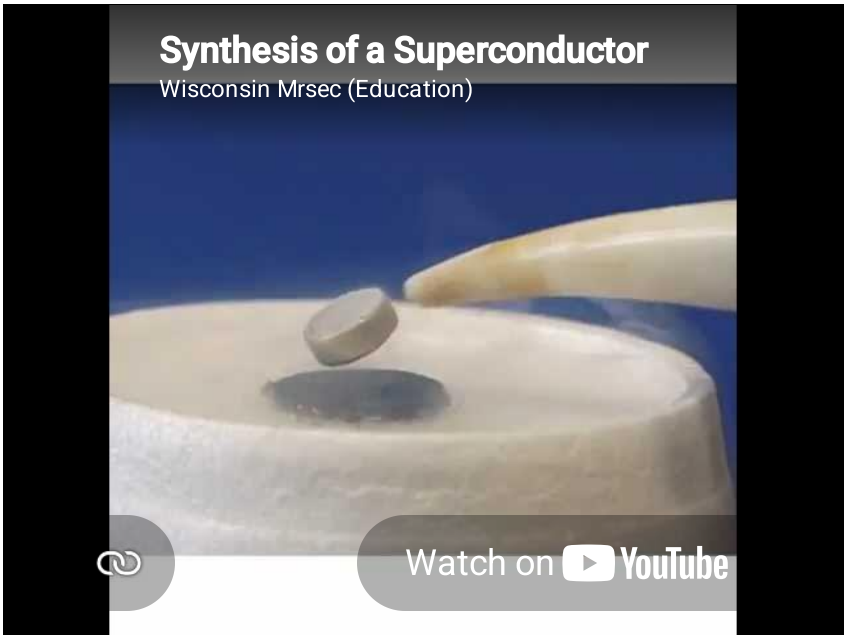
Unfortunately, for many years the only superconductors known had serious limitations, especially the need for very low temperatures, which required the use of expensive cryogenic fluids such as liquid He. In addition, the superconducting properties of many substances are destroyed by large electrical currents or even moderately large magnetic fields, making them useless for applications in power cables or high-field magnets. The ability of materials such as NbTi, NbSn, $Nb_3Si$, and $Nb_3Ge$ to tolerate rather high magnetic fields, however, has led to a number of commercial applications of superconductors, including high-field magnets for nuclear magnetic resonance (NMR) spectrometers and magnetic resonance imaging (MRI) instruments in medicine, which, unlike x-rays, can detect small changes in soft tissues in the body.

## High-Temperature Superconductors

Because of these limitations, scientists continued to search for materials that exhibited superconductivity at temperatures greater than 77 K (the temperature of liquid nitrogen, the least expensive cryogenic fluid). In 1986, Johannes G. Bednorz and Karl A. Müller, working for IBM in Zurich, showed that certain mixed-metal oxides containing La, Ba, and Cu exhibited superconductivity above 30 K. These compounds had been prepared by French workers as potential solid catalysts some years earlier, but their electrical properties had never been examined at low temperatures. Although initially the scientific community was extremely skeptical, the compounds were so easy to prepare that the results were confirmed within a few weeks. These high-temperature superconductorsA material that becomes a superconductor at temperatures greater than 30 K. earned Bednorz and Müller the Nobel Prize in Physics in 1987. Subsequent research has produced new compounds with related structures that are superconducting at temperatures as high as 135 K. The best known of these was discovered by Paul Chu and Maw-Kuen Wu Jr. and is called the "Chu–Wu phase" or the 1-2-3 superconductor.

The formula for the 1-2-3 superconductor is $YBa_2Cu_3O_{7-x}$, where $x$ is about 0.1 for samples that superconduct at about 95 K. If $x \approx 1.0$, giving a formula of $YBa_2Cu_3O_6$, the material is an electrical insulator. The superconducting phase is thus a nonstoichiometric compound, with a fixed ratio of metal atoms but a variable oxygen content. The overall equation for the synthesis of this material is as follows:

$$Y_2O_3\,(s) + 4BaCO_3\,(s) + 6CuO\,(s) + \frac{1}{2}O_2\,(g) \xrightarrow{\Delta} 2YBa_2Cu_3O_{7(s)} + 4CO_2\,(g) \tag{12.7.2}$$






If we assume that the superconducting phase is really stoichiometric $YBa_2Cu_3O_7$, then the average oxidation states of O, Y, Ba, and Cu are −2, +3, +2, and +7/3 respectively. The simplest way to view the average oxidation state of Cu is to assume that two Cu atoms per formula unit are present as $Cu^{2+}$ and one is present as the rather unusual $Cu^{3+}$. In $YBa_2Cu_3O_6$, the insulating form, the oxidation state of Cu is+5/3 so there are two $Cu^{2+}$ and one $Cu^{+}$ per formula unit.

As shown in Figure 12.7.3, the unit cell of the 1-2-3 superconductor is related to the unit cell of the simple perovskite structure (part (b) in Figure 12.7.3). The only difference between the superconducting and insulating forms of the compound is that an O atom has been removed from between the $Cu^{3+}$ ions, which destroys the chains of Cu atoms and leaves the Cu in the center of the unit cell as $Cu^{+}$. The chains of Cu atoms are crucial to the formation of the superconducting state.

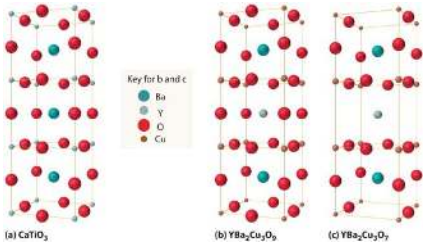



Figure 12.3.5) together with (b) replacement of all Ti atoms by Cu, replacement of Ca in the top and bottom cubes by Ba, and replacement of Ca in the central cube by Y gives a $YBa_2Cu_3O_9$ stoichiometry. (c) The removal of two oxygen atoms per unit cell gives the nominal $YBa_2Cu_3O_7$ stoichiometry of the superconducting material.

Table 12.7.1 lists the ideal compositions of some of the known high-temperature superconductors that have been discovered in recent years. Engineers have learned how to process the brittle polycrystalline 1-2-3 and related compounds into wires, tapes, and films that can carry enormous electrical currents. Commercial applications include their use in infrared sensors and in analog signal processing and microwave devices.

**Table 12.7.1** The Composition of Various Superconductors

| Compound | $T_c$ (K) |
|---|---|
| $Ba(Pb_{1-x}Bi_x)O_3$ | 13.5 |
| $(La_{2-x}Sr_x)CuO_4$ | 35 |
| $YBa_2Cu_3O_{7-x}$ | 95 |
| $Bi_2(Sr_{2-x}Ca_x)CuO_6$* | 80 |
| $Bi_2Ca_2Sr_2Cu_3O_{10}$* | 110 |
| $Tl_2Ba_2Ca_2Cu_3O_{10}$* | 125 |
| $HgBa_2Ca_2Cu_3O_8$* | 133 |
| $K_3C_{60}$ | 18 |
| $Rb_3C_{60}$ | 30 |
| *Nominal compositions only. Oxygen deficiencies or excesses are common in these compounds. | |

## Example 12.7.1

Calculate the average oxidation state of Cu in a sample of $YBa_2Cu_3O_{7-x}$ with $x$ = 0.5. How do you expect its structure to differ from those shown in Figure 12.7.3 for $YBa_2Cu_3O_9$ and $YBa_2Cu_3O_7$?

**Given:** stoichiometry

**Asked for:** average oxidation state and structure

**Strategy:**

**A** Based on the oxidation states of the other component atoms, calculate the average oxidation state of Cu that would make an electrically neutral compound.

**B** Compare the stoichiometry of the structures shown in Figure 12.7.3 with the stoichiometry of the given compound to predict how the structures differ.

**Solution:**

**A** The net negative charge from oxygen is (7.0 − 0.5) (−2) = −13, and the sum of the charges on the Y and Ba atoms is [1 × (+3)] + [2 × (+2)] = +7. This leaves a net charge of −6 per unit cell, which must be compensated for by the three Cu atoms, for a net charge of <math display="inline" xml:id="av_1.0-ch12_m033"><semantics><mrow><mo>+</mo><mfrac><mn>6</mn><mn>3</mn></mfrac><mo>=</mo><mo>+</mo><mn>2</mn></mrow></semantics></math> per Cu.

**B** The most likely structure would be one in which every other O atom between the Cu atoms in the Cu chains of $YBa_2Cu_3O_7$ has been removed.

Exercise

Calculate the average oxidation state of Cu in a sample of $HgBa_2Ca_2Cu_3O_8$. Assume that Hg is present as $Hg^{2+}$.

**Answer:** +2

## Summary

**Superconductors** are solids that at low temperatures exhibit zero resistance to the flow of electrical current, a phenomenon known as **superconductivity**. The temperature at which the electrical resistance of a substance drops to zero is its **superconducting transition temperature ($T_c$)**. Superconductors also expel a magnetic field from their interior, a phenomenon known as the **Meissner effect**. Superconductivity can be explained by the **BCS theory**, which says that electrons are able to travel through a solid with no resistance because they couple to form pairs of electrons (Cooper pairs). **High-temperature superconductors** have $T_c$ values greater than 30 K.

## Key Takeaway

- Superconductivity can be described using the BCS theory, in which Cooper pairs of electrons migrate through the crystal as a unit.

## Conceptual Problems

1. Why does the BCS theory predict that superconductivity is not possible at temperatures above approximately 30 K?
2. How does the formation of Cooper pairs lead to superconductivity?

## Answer

1. According to BCS theory, the interactions that lead to formation of Cooper pairs of electrons are so weak that they should be disrupted by thermal vibrations of lattice atoms above about 30 K.
2.

## Contributors

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Video from Wisconsin MRSEC @ YouTube

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# 12.8: Polymers

**Learning Objectives**

- To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called polymersA giant molecule that consists of many basic structural units (monomers) connected in a chain or network by covalent bonds. (from the Greek *poly* and *meros*, meaning “many parts”). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses. They consist of basic structural units called monomersThe basic structural unit of a polymer., which are repeated many times in each molecule. As shown schematically in Figure 12.8.1 , polymerizationA process by which monomers are connected into chains or networks by covalent bonds. is the process by which monomers are connected into chains or networks by covalent bonds. Polymers can form via a *condensation reaction*, in which two monomer molecules are joined by a new covalent bond and a small molecule such as water is eliminated, or by an *addition reaction*, a variant of a condensation reaction in which the components of a species AB are added to adjacent atoms of a multiple bond. (For more information about condensation and addition reactions, see Section 7.5.) Many people confuse the terms *plastics* and *polymers*. PlasticThe property of a material that allows it to be molded into almost any shape. is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

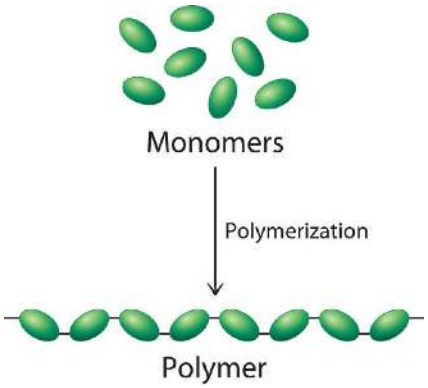


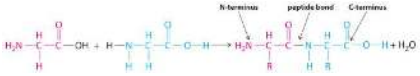

Figure 12.8.1Polymer Formation During a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.

### Note the Pattern

Polymers are formed via condensation or addition reactions.

## Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where $H_2O$ is eliminated:



In the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-terminus*). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:




The most important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. Chains with less than about 50 amino acid residues are called peptidesBiological polymers with less than about 50 amino acid residues., whereas those with more than about 50 amino acid residues are called proteinsBiological polymers with more than 50 amino acid residues linked together by amide bonds.. Many proteins are enzymesCatalysts that occur naturally in living organisms and that catalyze biological reactions., which are catalysts that increase the rate of a biological reaction.

### Note the Pattern

Synthetic polymers usually contain only a few different monomers, whereas biological polymers can have many kinds of monomers, such as amino acids arranged in different orders.

Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain. Other important peptides are the hormones vasopressin and oxytocin. Although their structures and amino acid sequences are similar, vasopressin is a blood pressure regulator, whereas oxytocin induces labor in pregnant women and milk production in nursing mothers. Oxytocin was the first biologically active peptide to be prepared in the laboratory by Vincent du Vigneaud (1901–1978), who was awarded the Nobel Prize in Chemistry in 1955.

## Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion (For more information on corrosion, see Section 19.6 .) In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 12.8.2). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibersA particle of a synthetic polymer that is more than 100 times longer than it is wide. that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible $–CH_2–$ units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

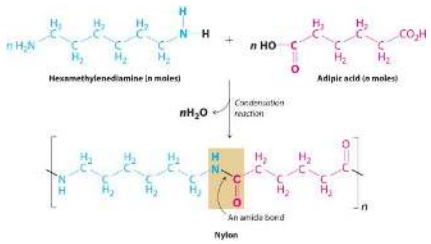



Figure 12.8.2 The Synthesis of Nylon Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.



**A fiberglass mat (left) and a Kevlar vest (right).**

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel.

Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene ($CH_2$=$CH_2$), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene (LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.

Because most synthetic fibers are neither soluble nor low melting, multistep processes are required to manufacture them and form them into objects. Graphite fibers are formed by heating a precursor polymer at high temperatures to decompose it, a process called pyrolysisA high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.. The usual precursor for graphite is polyacrylonitrile, better known by its trade name—Orlon. A similar approach is used to prepare fibers of silicon carbide using an organosilicon precursor such as polydimethylsilane $\{[–(CH_3)_2Si–]_n\}$. A new type of fiber consisting of carbon nanotubes, hollow cylinders of carbon just one atom thick, is lightweight, strong, and impact resistant. Its performance has been compared to that of Kevlar, and it is being considered for use in body armor, flexible solar panels, and bombproof trash bins, among other uses.

Because there are no good polymer precursors for elemental boron or boron nitride, these fibers have to be prepared by time-consuming and costly indirect methods. Even though boron fibers are about eight times stronger than metallic aluminum and 10% lighter, they are significantly more expensive. Consequently, unless an application requires boron's greater resistance to oxidation, these fibers cannot compete with less costly graphite fibers.

### Example 12.8.1

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

**Given:** type of polymer

**Asked for:** application

**Strategy:**

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

**Solution:**

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

Exercise

Which products are manufactured from LDPE and which from HPDE?

1. lawn chair frames
2. rope
3. disposable syringes
4. automobile protective covers

**Answer**

1. HDPE
2. LDPE
3. HDPE
4. LDPE

## Summary

**Polymers** are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

## Key Takeaway

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or synthetic polymers.

## Conceptual Problems

1. How are amino acids and proteins related to monomers and polymers? Draw the general structure of an amide bond linking two amino acid residues.
2. Although proteins and synthetic polymers (such as nylon) both contain amide bonds, different terms are used to describe the two types of polymer. Compare and contrast the terminology used for the
    1. smallest repeating unit.
    2. covalent bond connecting the units.

## Contributors

- Anonymous

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# 12.9: Modern Materials

**Learning Objectives**

- To become familiar with the properties of some contemporary materials.

In addition to polymers, other materials, such as ceramics, high-strength alloys, and composites, play a major role in almost every aspect of our lives. Until relatively recently, steel was used for any application that required an especially strong and durable material, such as bridges, automobiles, airplanes, golf clubs, and tennis rackets. In the last 15 to 20 years, however, graphite or boron fiber golf clubs and tennis rackets have made wood and steel obsolete for these items. Likewise, a modern jet engine now is largely composed of Ti and Ni by weight rather than steel (Table 12.9.1). The percentage of iron in wings and fuselages is similarly low, which indicates the extent to which other materials have supplanted steel. The Chevrolet Corvette introduced in 1953 was considered unusual because its body was constructed of fiberglass, a composite material, rather than steel; by 1992, Jaguar fabricated an all-aluminum limited-edition vehicle. In fact, the current models of many automobiles have engines that are made mostly of aluminum rather than steel. In this section, we describe some of the chemistry behind three classes of contemporary materials: ceramics, superalloys, and composites.

Table 12.9.1 The Approximate Elemental Composition of a Modern Jet Engine

| Element | Percentage by Mass |
|---|---|
| titanium | 38 |
| nickel | 37 |
| chromium | 12 |
| cobalt | 6 |
| aluminum | 3 |
| niobium | 1 |
| tantalum | 0.025 |

## Ceramics

A ceramic is any nonmetallic, inorganic solid that is strong enough for use in structural applications. Traditional ceramics, which are based on metal silicates or aluminosilicates, are the materials used to make pottery, china, bricks, and concrete. Modern ceramics contain a much wider range of components and can be classified as either *ceramic oxides*, which are based on metal oxides such as alumina ($Al_2O_3$), zirconia ($ZrO_2$), and beryllia (BeO), or *nonoxide ceramics*, which are based on metal carbides such as silicon carbide (carborundum, SiC) and tungsten carbide (WC), or nitrides like silicon nitride ($Si_3N_4$) and boron nitride (BN).

All modern ceramics are hard, lightweight, and stable at very high temperatures. Unfortunately, however, they are also rather brittle, tending to crack or break under stresses that would cause metals to bend or dent. Thus a major challenge for materials scientists is to take advantage of the desirable properties of ceramics, such as their thermal and oxidative stability, chemical inertness, and toughness, while finding ways to decrease their brittleness to use them in new applications. Few metals can be used in jet engines, for example, because most lose mechanical strength and react with oxygen at the very high operating temperatures inside the engines (approximately 2000°C). In contrast, ceramic oxides such as $Al_2O_3$ cannot react with oxygen regardless of the temperature because aluminum is already in its highest possible oxidation state ($Al^{3+}$). Even nonoxide ceramics such as silicon and boron nitrides and silicon carbide are essentially unreactive in air up to about 1500°C. Producing a high-strength ceramic for service use involves a process called sintering, which fuses the grains into a dense and strong material (Figure 12.9.2).

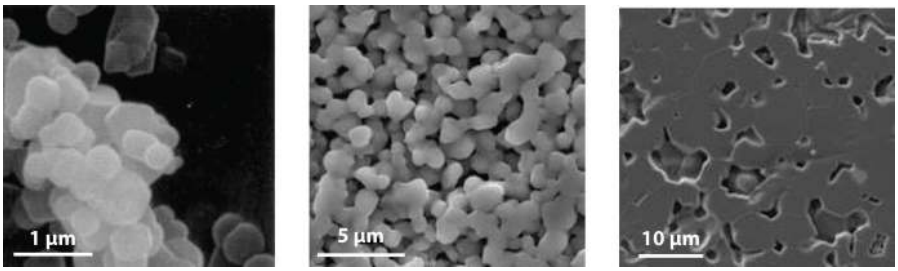



Figure 12.9.2: Sintering These photos show the effects of sintering magnesium oxide grains: (a) the microstructure before sintering; (b) the microstructure of the ceramic after sintering for two hours at 1250°C; and (c) the microstructure after sintering for two hours at 1450°C. During the sintering process, the grains fuse, forming a dense and strong material.

> *Ceramics are hard, lightweight, and able to withstand high temperatures, but they are also brittle.*

One of the most widely used raw materials for making ceramics is clay. Clay minerals consist of hydrated alumina ($Al_2O_3$) and silica ($SiO_2$) that have a broad range of impurities, including barium, calcium, sodium, potassium, and iron. Although the structures of clay minerals are complicated, they all contain layers of metal atoms linked by oxygen atoms. Water molecules fit between the layers to form a thin film of water. When hydrated, clays can be easily molded, but during high-temperature heat treatment, called *firing*, a dense and strong ceramic is produced.

Because ceramics are so hard, they are easily contaminated by the material used to grind them. In fact, the ceramic often grinds the metal surface of the mill almost as fast as the mill grinds the ceramic! The sol-gel process was developed to address this problem. In this process, a water-soluble precursor species, usually a metal or semimetal alkoxide [$M(OR)_n$] undergoes a hydrolysis reaction to form a cloudy aqueous dispersion called a *sol*. The sol contains particles of the metal or semimetal hydroxide [$M(OH)_n$], which are typically 1–100 nm in diameter. As the reaction proceeds, molecules of water are eliminated from between the $M(OH)_n$ units in a condensation reaction, and the particles fuse together, producing oxide bridges, M–O–M. Eventually, the particles become linked in a three-dimensional network that causes the solution to form a *gel*, similar to a gelatin dessert. Heating the gel to 200°C–500°C causes more water to be eliminated, thus forming small particles of metal oxide that can be amazingly uniform in size. This chemistry starts with highly pure $SiCl_4$ and proceeds via the following reactions starting with the alkoxide formation

$$SiCl_4\,(s) + 4CH_3CH_2OH\,(l) + 4NH_3\,(g) \rightarrow SiO\,(OCH_2CH_3)_4\,(s) + 4NH_4Sl\,(s) \tag{12.9.1}$$

and then the hydrolysis of the alkoxide

$$SiO\,(OCH_2CH_3)_4\,(s) + 4H_2O\,(l) \rightarrow (HO)_3\,Si - OH\,(s) + 4CH_3CH_2OH\,(aq) \tag{12.9.2}$$

ending with the condensation

$$\begin{gathered}(HO_3)\,Si - OH\,(s) + nHO - Si\,(OH)_3\,(s) \\ \rightarrow (HO_3)\,Si\,(-O - Si\,(OH)_3)_n\,(s) + nH_2O\,(l)\end{gathered} \tag{12.9.3}$$

Nature uses the same process to create opal gemstones.

## Superalloys

Superalloys are high-strength alloys, often with a complex composition, that are used in systems requiring mechanical strength, high surface stability (minimal flaking or pitting), and resistance to high temperatures. The aerospace industry, for example, requires materials that have high strength-to-weight ratios to improve the fuel efficiency of advanced propulsion systems, and these systems must operate safely at temperatures greater than 1000°C.

> *Superalloys are used in systems requiring mechanical strength, minimal flaking or pitting, and high-temperature resistance.*

Although most superalloys are based on nickel, cobalt, or iron, other metals are used as well. Pure nickel or cobalt is relatively easily oxidized, but adding small amounts of other metals (Al, Co, Cr, Mo, Nb, Ti, and W) results in an alloy that has superior properties. Consequently, most of the internal parts of modern gas turbine jet engines are now made of superalloys based on either

nickel (used in blades and disks) or cobalt (used in vanes, combustion chamber liners, and afterburners). The cobalt-based superalloys are not as strong as the nickel-based ones, but they have excellent corrosion resistance at high temperatures.

Other alloys, such as aluminum–lithium and alloys based on titanium, also have applications in the aerospace industry. Because aluminum–lithium alloys are lighter, stiffer, and more resistant to fatigue at high temperatures than aluminum itself, they are used in engine parts and in the metal "skins" that cover wings and bodies. Titanium's high strength, corrosion resistance, and lightweight properties are equally desirable for applications where minimizing weight is important (as in airplanes). Unfortunately, however, metallic titanium reacts rapidly with air at high temperatures to form TiN and $TiO_2$. The welding of titanium or any similar processes must therefore be carried out in an argon or inert gas atmosphere, which adds significantly to the cost. Initially, titanium and its alloys were primarily used in military applications, but more recently, they have been used as components of the airframes of commercial planes, in ship structures, and in biological implants.

## Composite Materials

Composite materials have at least two distinct components: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix and limit the growth of cracks by pinning defects in the bulk material (Figure 12.9.3). The resulting material is stronger, tougher, stiffer, and more resistant to corrosion than either component alone. Composites are thus the nanometer-scale equivalent of reinforced concrete, in which steel rods greatly increase the mechanical strength of the cement matrix, and are extensively used in the aircraft industry, among others. For example, the Boeing 777 is 9% composites by weight, whereas the newly developed Boeing 787 is 50% composites by weight. Not only does the use of composite materials reduce the weight of the aircraft, and therefore its fuel consumption, but it also allows new design concepts because composites can be molded. Moreover, by using composites in the Boeing 787 multiple functions can be integrated into a single system, such as acoustic damping, thermal regulation, and the electrical system.

Three distinct types of composite material are generally recognized, distinguished by the nature of the matrix. These are polymer-matrix composites, metal-matrix composites, and ceramic-matrix composites.

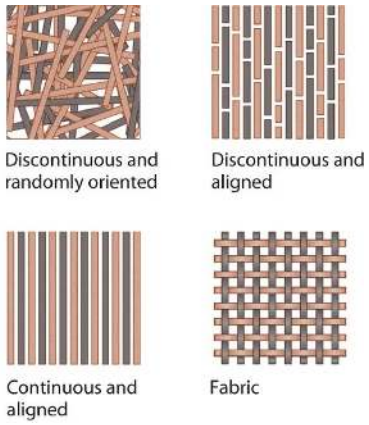



Figure 12.9.3: Some Possible Arrangements of Fibers in Fiber-Reinforced Composite Materials The arrangements shown range from discontinuous and randomly oriented to continuous and aligned. The fibers limit the growth of cracks by pinning defects within the matrix.

> *Composites are stronger, tougher, stiffer, and more resistant to corrosion than their components alone.*

Fiberglass is a polymer-matrix composite that consists of glass fibers embedded in a polymer, forming tapes that are then arranged in layers impregnated with epoxy. The result is a strong, stiff, lightweight material that is resistant to chemical degradation. It is not strong enough, however, to resist cracking or puncturing on impact. Stronger, stiffer polymer-matrix composites contain fibers of carbon (graphite), boron, or polyamides such as Kevlar. High-tech tennis rackets and golf clubs as well as the skins of modern military aircraft such as the "stealth" F-117A fighters and B-2 bombers are made from both carbon fiber–epoxy and boron fiber–epoxy composites. Compared with metals, these materials are 25%–50% lighter and thus reduce operating costs. Similarly, the space shuttle payload bay doors and panels are made of a carbon fiber–epoxy composite. The structure of the Boeing 787 has been

described as essentially one giant macromolecule, where everything is fastened through cross-linked chemical bonds reinforced with carbon fiber.

Metal-matrix composites consist of metals or metal alloys reinforced with fibers. They offer significant advantages for high-temperature applications but pose major manufacturing challenges. For example, obtaining a uniform distribution and alignment of the reinforcing fibers can be difficult, and because organic polymers cannot survive the high temperatures of molten metals, only fibers composed of boron, carbon, or ceramic (such as silicon carbide) can be used. Aluminum alloys reinforced with boron fibers are used in the aerospace industry, where their strength and lightweight properties make up for their relatively high cost. The skins of hypersonic aircraft and structural units in the space shuttle are made of metal-matrix composites.

Ceramic-matrix composites contain ceramic fibers in a ceramic matrix material. A typical example is alumina reinforced with silicon carbide fibers. Combining the two very high-melting-point materials results in a composite that has excellent thermal stability, great strength, and corrosion resistance, while the SiC fibers reduce brittleness and cracking. Consequently, these materials are used in very high-temperature applications, such as the leading edge of wings of hypersonic airplanes and jet engine parts. They are also used in the protective ceramic tiles on the space shuttle, which contain short fibers of pure $SiO_2$ mixed with fibers of an aluminum–boron–silicate ceramic. These tiles are excellent thermal insulators and extremely light (their density is only about 0.2 $g/cm^3$). Although their surface reaches a temperature of about 1250°C during reentry into Earth's atmosphere, the temperature of the underlying aluminum alloy skin stays below 200°C.

### Example 12.9.1:

An engineer is tasked with designing a jet ski hull. What material is most suited to this application? Why?

**Given:** design objective

**Asked for:** most suitable material

**Strategy:**

Determine under what conditions the design will be used. Then decide what type of material is most appropriate.

**Solution:**

A jet ski hull must be lightweight to maximize speed and fuel efficiency. Because of its use in a marine environment, it must also be resistant to impact and corrosion. A ceramic material provides rigidity but is brittle and therefore tends to break or crack under stress, such as when it impacts waves at high speeds. Superalloys provide strength and stability, but a superalloy is probably too heavy for this application. Depending on the selection of metals, it might not be resistant to corrosion in a marine environment either. Composite materials, however, provide strength, stiffness, and corrosion resistance; they are also lightweight materials. This is not a high-temperature application, so we do not need a metal-matrix composite or a ceramic-matrix composite. The best choice of material is a polymer-matrix composite with Kevlar fibers to increase the strength of the composite on impact.

### Exercise 12.9.1

In designing a new generation of space shuttle, National Aeronautics and Space Administration (NASA) engineers are considering thermal-protection devices to protect the skin of the craft. Among the materials being considered are titanium- or nickel-based alloys and silicon-carbide ceramic reinforced with carbon fibers. Why are these materials suitable for this application?

**Answer:** Ti- or Ni-based alloys have a high strength-to-weight ratio, resist corrosion, and are safe at high temperatures. Reinforced ceramic is lightweight; has high thermal and oxidative stability; and is chemically inert, tough, and impact resistant.

## Summary

**Ceramics** are nonmetallic, inorganic solids that are typically strong; they have high melting points but are brittle. The two major classes of modern ceramics are ceramic oxides and nonoxide ceramics, which are composed of nonmetal carbides or nitrides. The production of ceramics generally involves pressing a powder of the material into the desired shape and sintering at a temperature

just below its melting point. The necessary fine powders of ceramic oxides with uniformly sized particles can be produced by the **sol-gel process**. **Superalloys** are new metal phases based on cobalt, nickel, or iron that exhibit unusually high temperature stability and resistance to oxidation. **Composite materials** consist of at least two phases: a matrix that constitutes the bulk of the material and fibers or granules that act as a reinforcement. **Polymer-matrix composites** have reinforcing fibers embedded in a polymer matrix. **Metal-matrix composites** have a metal matrix and fibers of boron, graphite, or ceramic. **Ceramic-matrix composites** use reinforcing fibers, usually also ceramic, to make the matrix phase less brittle.

## Key Takeaway

- Materials that have contemporary applications include ceramics, high-strength alloys, and composites, whose properties can be modified as needed.

## Conceptual Problems

1. Can a compound based on titanium oxide qualify as a ceramic material? Explain your answer.
2. What features make ceramic materials attractive for use under extreme conditions? What are some potential drawbacks of ceramics?
3. How do composite materials differ from the other classes of materials discussed in this chapter? What advantages do composites have versus other materials?
4. How does the matrix control the properties of a composite material? What is the role of an additive in determining the properties of a composite material?

## Contributors

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# CHAPTER OVERVIEW

## 13: Solutions

We explored the general properties of gases, liquids, and solids. Most of the discussion focused on pure substances containing a single kind of atom, molecule, or cation–anion pair. The substances we encounter in our daily lives, however, are usually mixtures rather than pure substances. Some are heterogeneous mixtures, which consist of at least two phases that are not uniformly dispersed on a microscopic scale; others are homogeneous mixtures, consisting of a single phase in which the components are uniformly distributed. Homogeneous mixtures are also called **solutions**; they include the air we breathe, the gas we use to cook and heat our homes, the water we drink, the gasoline or diesel fuel that powers engines, and the gold and silver jewelry we wear.


13.1: Factors Affecting Solution Formation
13.2: Solubility and Molecular Structure
13.3: Units of Concentration
13.4: Effects of Temperature and Pressure on Solubility
13.5: Colligative Properties of Solutions
13.6: Aggregate Particles
13.7: Aggregate Particles in Aqueous Solution


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# 13.1: Factors Affecting Solution Formation

**Learning Objectives**

- to understand how enthalpy and entropy changes affect solution formation.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table 13.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

**Table 13.1:** Types of Solutions

| Solution | Solute | Solvent | Examples |
|---|---|---|---|
| gas | gas | gas | air, natural gas |
| liquid | gas | liquid | seltzer water ($CO_2$ gas in water) |
| liquid | liquid | liquid | alcoholic beverage (ethanol in water), gasoline |
| liquid | solid | liquid | tea, salt water |
| solid | gas | solid | $H_2$ in Pd (used for $H_2$ storage) |
| solid | solid | liquid | mercury in silver or gold (amalgam often used in dentistry) |

## Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$Zn(NO_3)_{2(s)} + H_2O(l) \rightarrow Zn^{2+}_{(aq)} + 2NO^{-}_{3(aq)} \tag{13.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$Zn_{(s)} + 2H^{+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + H_{2(g)} \tag{13.2}$$

Note

*Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Substances that form a single homogeneous phase in all proportions are said to be completely miscible in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are immiscible. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

## The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation, or hydration when the solvent is water. Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by $\Delta H_1$, $\Delta H_2$, and $\Delta H_3$ in Figure 13.1. The overall enthalpy change in the formation of the solution ($\Delta H_{soln}$) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{13.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent ($\Delta H_1$) and the solute ($\Delta H_2$). Because $\Delta H$ is positive for both steps 1 and 2, the solute–solvent interactions ($\Delta H_3$) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as $MgO$ (−3791 kJ/mol), are generally insoluble in all solvents.

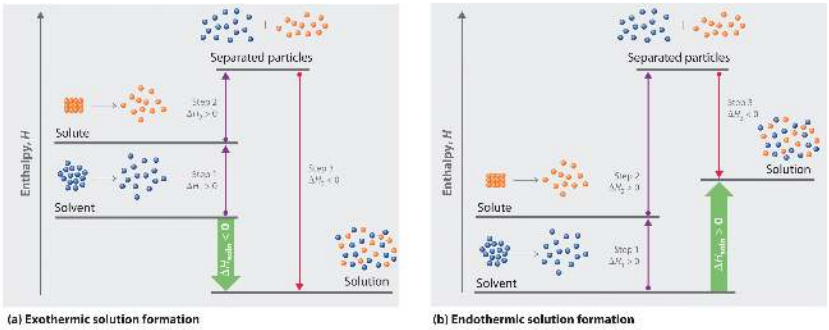



Figure 13.1: Enthalpy Changes That Accompany the Formation of a Solution. *Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When $\Delta H_3$ is larger in magnitude than the sum of $\Delta H_1$ and $\Delta H_2$, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When $\Delta H_3$ is smaller in magnitude than the sum of $\Delta H_1$ and $\Delta H_2$, the overall process is endothermic (ΔHsoln > 0).*

A positive value for $\Delta H_{soln}$ does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high $\Delta H_{soln}$ is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive $\Delta H_{soln}$ of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 13.2).




Figure 13.2: Commercial Cold Packs for Treating Injuries. *These packs contain solid $NH_4NO_3$ and water in separate compartments. When the seal between the compartments is broken, the $NH_4NO_3$ dissolves in the water. Because $\Delta H_{soln}$ for $NH_4NO_3$ is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.*

## Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detailelsehwere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, is arbitrarily assigned an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔHsoln should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative $\Delta H_{soln}$ but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

| Note |
| --- |
| *All spontaneous processes with ΔH ≥ 0 are characterized by an increase in entropy.* |

Table 13.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

**Table 13.2:** Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

| $\Delta H_1$ (separation of solvent molecules) | $\Delta H_2$ (separation of solute particles) | $\Delta H_3$ (solute–solvent interactions) | $\Delta H_{soln}$ ($\Delta H_1 + \Delta H_2 + \Delta H_3$) | Result of Mixing Solute and Solvent[†] |
|---|---|---|---|---|
| large; positive | large; positive | large; negative | small; positive or negative | solution will usually form |
| small; positive | large; positive | small; negative | large; positive | solution will not form |
| large; positive | small; positive | small; negative | large; positive | solution will not form |
| small; positive | small; positive | small; negative | small; positive or negative | solution will usually form |

*$\Delta H_1$, $\Delta H_2$, and $\Delta H_3$ refer to the processes indicated in the thermochemical cycle shown in Figure 13.1.

[†]In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 13.3). Consequently, all gases dissolve readily in one another in all proportions to form solutions. We will return to a discussion of enthalpy and entropy in Chapter 18, where we treat their relationship quantitatively.

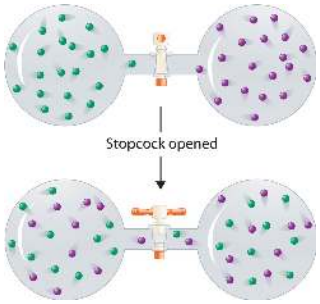



Figure 13.3 Formation of a Solution of Two Gases. *(top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔHsoln is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.*

Example 13.1

Considering LiCl, benzoic acid ($C_6H_5CO_2H$), and naphthalene, which will be most soluble and which will be least soluble in water?

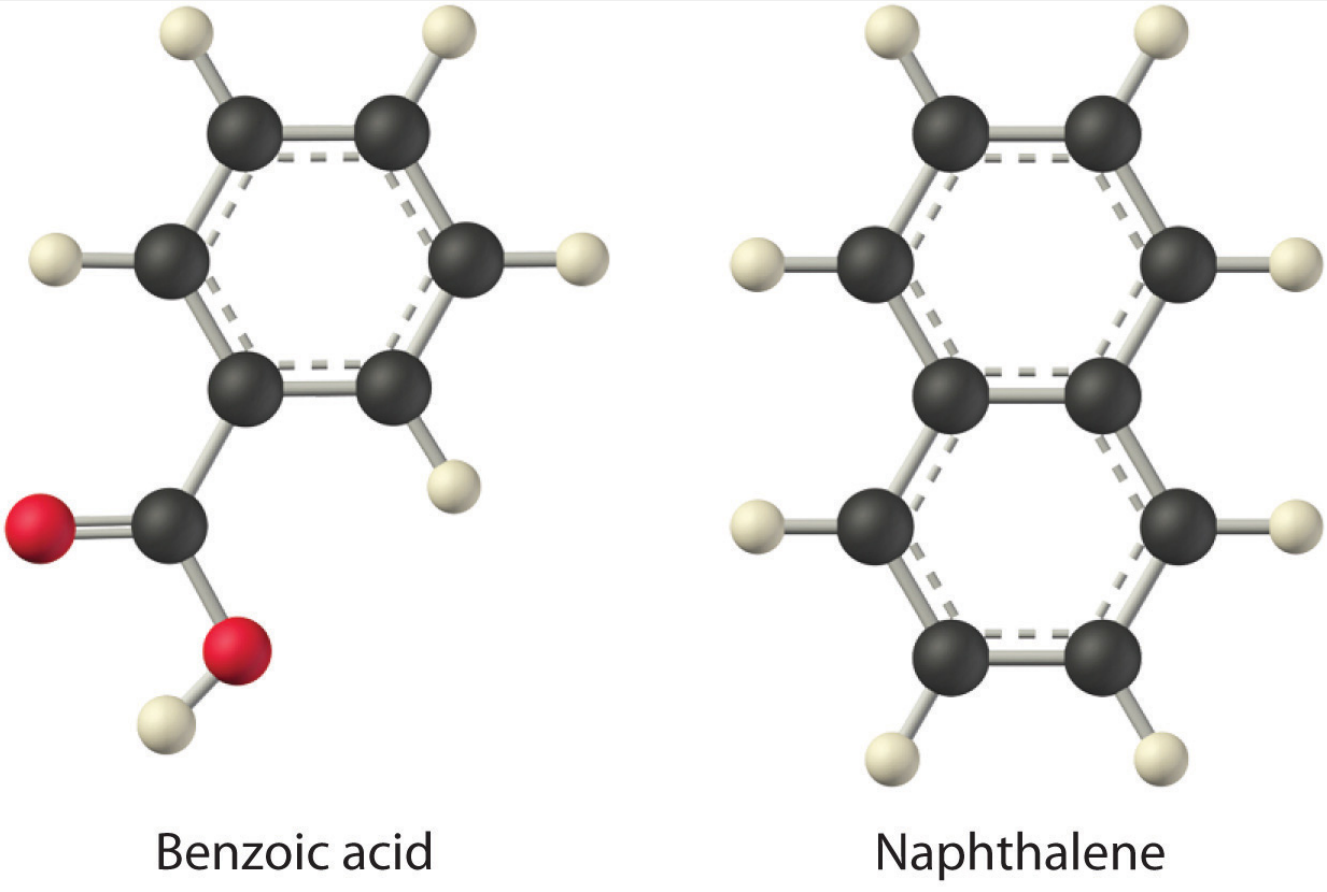
**Given**: three compounds

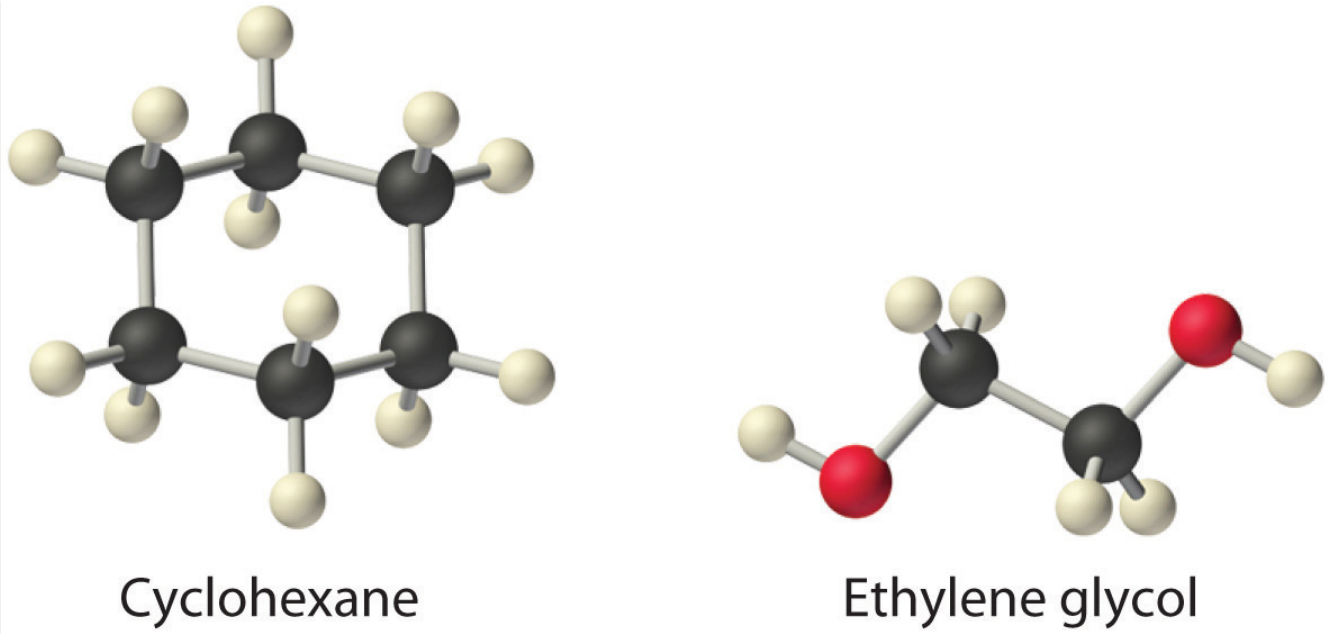
**Asked for:** relative solubilities in water

**Strategy**: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 13.1. Then use Table 13.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

**Solution**:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy ($\Delta H_2$ is far greater than zero in Equation 13.3). Because water is a polar substance, the interactions between both $Li^+$ and $Cl^-$ ions and water should be favorable and strong. Thus we expect $\Delta H_3$ to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect $\Delta H_2$ to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules ($\Delta H_2$) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.






**Exercise**

Exercise 13.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?

**Solution**

The most soluble is cyclohexane; the least soluble is ammonium chloride.

## Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, $\Delta H_{soln}$, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

## Key Takeaway

The magnitude of the changes in both enthalpy and entropy must be considered when predicting whether a given solute–solvent combination will spontaneously form a solution.

## Conceptual Problems

1. Classify each of the following as a heterogeneous mixture or homogeneous mixture. Explain your rationale in each case.

    a. aqueous ammonia

    b. liquid decongestant

    c. vinegar

d. seawater

e. gasoline

f. fog

2. Solutions and heterogeneous mixtures are at the extreme ends of the solubility scale. Name one type of mixture that is intermediate on this scale. How are the properties of the mixture you have chosen different from those of a solution or a heterogeneous mixture?

3. Classify each process as simple dissolution or a chemical reaction.

a. a naphthalene mothball dissolving in benzene

b. a sample of a common drain cleaner that has a mixture of NaOH crystals and Al chunks dissolving in water to give H2 gas and an aqueous solution of $Na^+$, $OH^-$, and $Al^{3+}$ ions

c. an iron ship anchor slowly dissolving in seawater

d. sodium metal dissolving in liquid ammonia

4. Classify each process as simple dissolution or a chemical reaction.

a. a sugar cube dissolving in a cup of hot tea

b. $SO_3$ gas dissolving in water to produce sulfuric acid

c. calcium oxide dissolving in water to produce a basic solution

d. metallic gold dissolving in a small quantity of liquid mercury

5. You notice that a gas is evolved as you are dissolving a solid in a liquid. Will you be able to recover your original solid by evaporation? Why or why not?

6. Why is heat evolved when sodium hydroxide pellets are dissolved in water? Does this process correspond to simple dissolution or a chemical reaction? Justify your answer.

7. Which process(es) is the simple formation of a solution, and which process(es) involves a chemical reaction?

a. mixing an aqueous solution of NaOH with an aqueous solution of HCl

b. bubbling HCl gas through water

c. adding iodine crystals to $CCl_4$

d. adding sodium metal to ethanol to produce sodium ethoxide ($C_2H_5O^-Na^+$) and hydrogen gas

8. Using thermochemical arguments, explain why some substances that do not form a solution at room temperature will form a solution when heated. Explain why a solution can form even when $\Delta H_{soln}$ is positive.

9. If you wanted to formulate a new compound that could be used in an instant cold pack, would you select a compound with a positive or negative value of $\Delta H_{soln}$ in water? Justify your answer.

10. Why is entropy the dominant factor in the formation of solutions of two or more gases? Is it possible for two gases to be immiscible? Why or why not?

## Answers

1. Homogeneous mixtures: aqueous ammonia, liquid decongestant, vinegar, and gasoline. Heterogeneous mixtures: seawater and fog.
2. All are chemical reactions except dissolving iodine crystals in $CCl_4$.

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# 13.2: Solubility and Molecular Structure

**Learning Objectives**

- To understand the relationship between solubility and molecular structure.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in Figure 13.4). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. Dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

$$\text{solute} + \text{solvent} \underset{\text{dissolution}}{\overset{\text{crystallization}}{\rightleftharpoons}} \text{solution} \tag{13.4}$$

Although the terms precipitation and crystallization are both used to describe the separation of solid solute from a solution, crystallization refers to the formation of a solid with a well-defined crystalline structure, whereas precipitation refers to the formation of any solid phase, often one with very small particles.

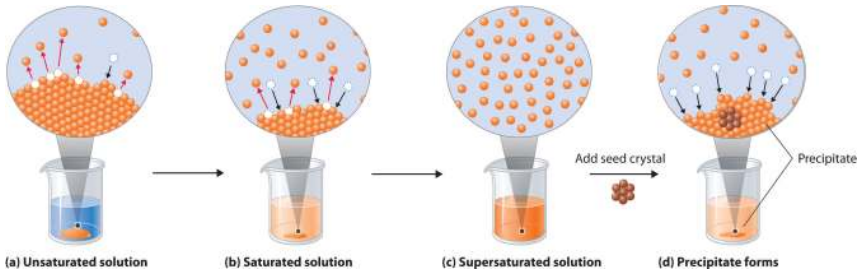



Figure 13.4 Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

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# 13.3: Units of Concentration

**Learning Objectives**

- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity was introduced in Chapter 4 as a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions, introduced in Chapter 10, are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 4 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 4

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

a. What is its molarity?

b. What is its mole fraction?

**Given**: mass of substance and mass and density of solution

**Asked for**: molarity and mole fraction

**Strategy**:

A. Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.

B. Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

**Solution**:

A The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass. The volume of the solution equals its mass divided by its density. The calculations follow:

$$moles\ CH_3CO_2H = \frac{3.78\ \cancel{g}\ CH_3CO_2H}{60.05\ \cancel{g}/mol} = 0.0629\ mol \tag{13.3.1}$$

$$volume = \frac{mass}{density} = \frac{100.0\ \cancel{g}\ solution}{1.00\ \cancel{g}/mL} = 100\ mL \tag{13.3.2}$$

$$molarity\ of\ CH_3CO_2H = \frac{moles\ CH_3CO_2H}{\text{liter solution}} = \frac{0.0629\ mol\ CH_3CO_2H}{(100\ \cancel{mL})(1\ L/1000\ \cancel{mL})} = 0.629\ M\ CH_3CO_2H \tag{13.3.3}$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than $\frac{1}{2}$ mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

B To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g − 3.78 g) = 96.2 g of water. We have

$$moles\ H_2O = \frac{96.2\ \cancel{g}\ H_2O}{18.02\ \cancel{g}/mol} = 5.34\ mol\ H_2O \tag{13.3.4}$$

The mole fraction $X$ of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$X_{CH_3CO_2H} = \frac{moles\ CH_3CO_2H}{moles\ CH_3CO_2H + moles\ H_2O} = \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol} = 0.0116 = 1.16 \times 10^{-2} \tag{13.3.5}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

Exercise 5

A solution of $HCl$ gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of $HCl$ per 100.0 g of solution, and its density is 1.10 g/mL.

a. What is its molarity?

b. What is its mole fraction?

**Answer**:

a. 6.10 M HCl

b. XHCl = 0.111

The concentration of a solution can also be described by its molality (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{13.5}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of $H_2O$ under these conditions is very close to 1.0 L, and a 0.50 M solution of $KBr$ in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentage, parts per million (ppm), or parts per billion (ppb):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{13.6}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{13.7}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{13.8}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of $H_2SO_4$ per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

Example 5

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?

b. What is the mass of benzene in the sample?

**Given**: volume of sample, solute concentration, and density of solution

**Asked for**: molarity of solute and mass of solute in 250 mL

**Strategy**:

A. Use the concentration of the solute in parts per million to calculate the molarity.

B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

**Solution**:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$molarity = \frac{moles}{litersolution} = \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} = 1.63 \times 10^{-4} M \tag{13.3.6}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$massofbenzene = \frac{(12.7\ mg\ benzene)(250\ \cancel{mL})}{1000\ mL} = 3.18\ mg = 3.18 \times 10^{-3}\ g\ benzene \tag{13.3.7}$$

Exercise 6

The maximum allowable concentration of lead in drinking water is 9.0 ppb. What is the molarity of $Pb^{2+}$ in a 9.0 ppb aqueous solution? Use your calculated concentration to determine how many grams of $Pb^{2+}$ are in an 8 oz glass of water.

**Answer**: 4.3 × 10−8 M; 2 × 10−6 g

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as we saw in Chapter 10. As you will learn in Section 13.5, mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 13.5 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 6.

**Table 13.5** Different Units for Expressing the Concentrations of Solutions*

| Unit | Definition | Application |
|---|---|---|
| molarity (M) | moles of solute/liter of solution (mol/L) | Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known. |
| mole fraction (X) | moles of solute/total moles present (mol/mol) | Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known. |
| molality (m) | moles of solute/kg of solvent (mol/kg) | Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known. |
| mass percentage (%) | [mass of solute (g)/mass of solution (g)] × 100 | Useful when masses are known but molecular masses are unknown. |
| parts per thousand (ppt) | [mass of solute/mass of solution] × 103 (g solute/kg solution) | Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000. |
| parts per million (ppm) | [mass of solute/mass of solution] × 106 (mg solute/kg solution) | Used for trace quantities; masses are known but molecular masses may be unknown. |
| parts per billion (ppb) | [mass of solute/mass of solution] × 109 (µg solute/kg solution) | Used for trace quantities; masses are known but molecular masses may be unknown. |

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Example 6

Vodka is essentially a solution of pure ethanol in water. Typical vodka is sold as “80 proof,” which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

**Given**: volume percent and density

**Asked for**: mass percentage, mole fraction, molarity, and molality

**Strategy**:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

**Solution**:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol ($CH_3CH_2OH$), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL}) \left( \frac{0.789\ g}{\cancel{mL}} \right) = 31.6\ g\ EtOH \tag{13.3.8}$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\%EtOH = \left( \frac{mass\ of\ EtOH}{mass\ of\ solution} \right) (100) = \left( \frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O} \right) (100) = 34.5\% \tag{13.3.9}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$moles\ EtOH = (31.6\ \cancel{g\ EtOH}) \left( \frac{1\ mol}{46.07\ \cancel{g\ EtOH}} \right) = 0.686\ mol\ CH_3CH_2OH \tag{13.3.10}$$

Similarly, the number of moles of water is

$$moles\ H_2O = (60.0\ \cancel{g\ H_2O}) \left( \frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} \right) = 3.33\ mol\ H_2O \tag{13.3.11}$$

The mole fraction of ethanol is thus

$$X_{EtOH} = \frac{0.686\ \cancel{mol}}{0.686\ \cancel{mol} + 3.33\ \cancel{mol}} = 0.171 \tag{13.3.12}$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{EtOH} = \left(\frac{0.686\ mol}{100\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{L}\right) = 6.86\ M \tag{13.3.13}$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{EtOH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m \tag{13.3.14}$$

Exercise 7

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

**Answer**:

a. mass percentage toluene = 24.8%
b. $X_{toluene} = 0.219$
c. 2.35 M toluene
d. 3.59 m toluene

## Contributors and Attributions

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# 13.4: Effects of Temperature and Pressure on Solubility

**Learning Objectives**

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

## Effect of Temperature on the Solubility of Solids

Figure 13.4.1 shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and $CH_3CO_2Na$) exhibit a dramatic increase in solubility with increasing temperature. Others (such as NaCl and $K_2SO_4$) exhibit little variation, and still others (such as $Li_2SO_4$) become less soluble with increasing temperature.

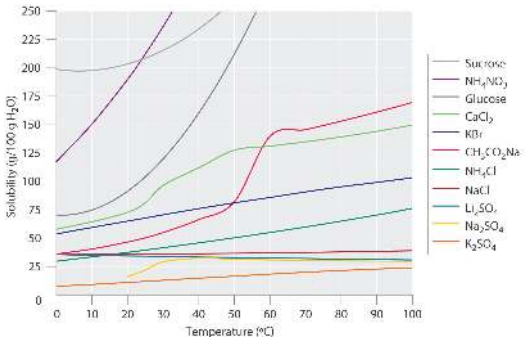



Figure 13.4.1: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-SA-NC; anonymous)

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, Li2SO4, Na2SO4, K2SO4.

Notice in particular the curves for $NH_4NO_3$ and $CaCl_2$. The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{soln} = +25.7\ kJ/mol$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{soln} = -68.2\ kJ/mol$), yet Figure 13.4.1 shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate ($CH_3CO_2Na$) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 13.4.1, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of $CH_3CO_2Na$ are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g − 36 g) of $CH_3CO_2Na$ crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original $CH_3CO_2Na$ in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 13.4.1 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be more soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

## Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 13.4.2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{soln} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas. The phenomenon is similar to that involved in the increase in the vapor pressure of a pure liquid with increasing temperature. In the case of vapor pressure, however, it is attractive forces between solvent molecules that are being overcome by the added thermal energy when the temperature is increased.

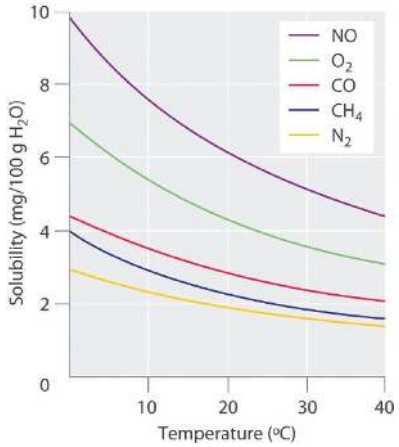



Figure 13.4.2: Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm. The solubilities of all gases decrease with increasing temperature. (CC BY-SA-NC; anonymous)

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called "boiler scale," a deposit that can seriously decrease the capacity of hot water pipes (Figure 13.4.3). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described elsewhere, but the driving force is the loss of dissolved $CO_2$ from solution. Hard water contains dissolved $Ca^{2+}$ and $HCO_3^-$ (bicarbonate) ions. Calcium bicarbonate ($Ca(HCO_3)_2$ is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$2\,HCO_3^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l) + CO_2(aq) \tag{13.4.1}$$

Heating the solution decreases the solubility of $CO_2$, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.



Figure 13.4.3: Calcium carbonate deposits (left) Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved $CO_2$ is driven into the gas phase at high temperatures. (right) Highly calcified remains of Eiffel aqueduct near Euskirchen-Kreuzweingarten, Germany. (Wikipedia)

### Thermal Pollution

In **thermal pollution**, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of $O_2$ at higher temperatures (Figure 13.4.2), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.



There are many causes of fish kill, but oxygen depletion is the most common cause. (Public Domain; United States Fish and Wildlife Service)

A similar effect is seen in the rising temperatures of bodies of water such as the k0oi89Chesapeake Bay, the largest estuary in North America, where \lobal warming has been implicated as the cause. For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelsgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

## Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 13.4.4, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

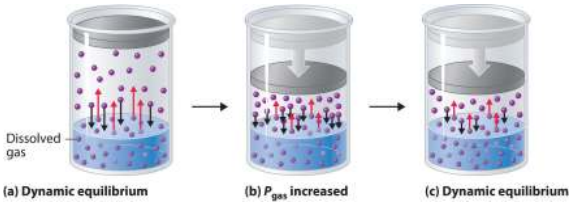



Figure 13.4.4: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established. (CC BY-SA-NC; anonymous)

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP \tag{13.4.2}$$

where

- $C$ is the concentration of dissolved gas at equilibrium,
- $P$ is the partial pressure of the gas, and
- $k$ is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 13.4.1.

As the data in Table 13.4.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the Group 18 elements, the Henry's law constants increase smoothly from He to Ne to Ar.

Table 13.4.1: Henry's Law Constants for Selected Gases in Water at 20°C

| Gas | Henry's Law Constant [mol/(L·atm)] × $10^{-4}$ |
|---|---|
| He | 3.9 |
| Ne | 4.7 |
| Ar | 15 |
| $H_2$ | 8.1 |
| $N_2$ | 7.1 |
| $O_2$ | 14 |
| $CO_2$ | 392 |

**Oxygen is Especially Soluble**

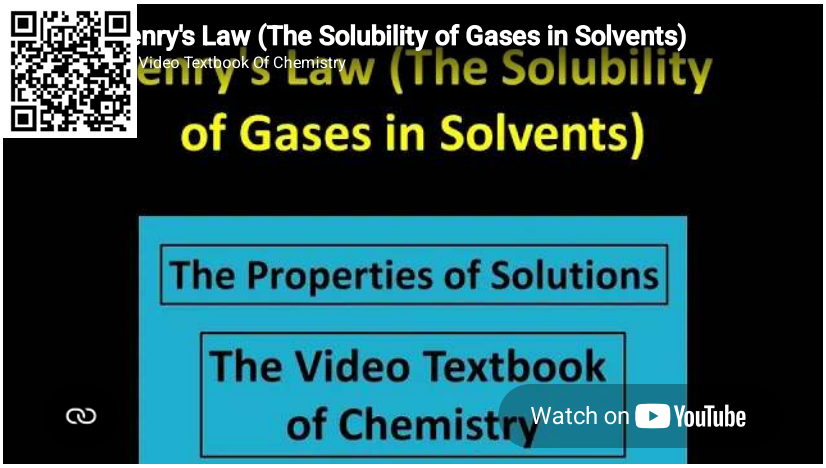
Nitrogen and oxygen are the two most prominent gases in the Earth's atmosphere and they share many similar physical properties. However, as Table 13.4.1 shows, $O_2$ is twice as soluble in water as $N_2$. Many factors contribute to solubility including the nature of the intermolecular forces at play. For a details discussion, see "The $O_2/N_2$ Ratio Gas Solubility Mystery" by Rubin Battino and Paul G. Seybold (J. Chem. Eng. Data 2011, 56, 5036–5044),

Gases that react chemically with water, such as HCl and the other hydrogen halides, $H_2S$, and $NH_3$, do **not** obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+(aq)$ and $Cl^-(aq)$, not dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

> *Gases that react with water do not obey Henry's law.*

Henry's law has important applications. For example, bubbles of $CO_2$ form as soon as a carbonated beverage is opened because the drink was bottled under $CO_2$ at a pressure greater than 1 atm. When the bottle is opened, the pressure of $CO_2$ above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of $N_2$ to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for $O_2$ in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the $O_2$ concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind $O_2$ reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds $O_2$ and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four $O_2$ molecules. Although the concentration of dissolved $O_2$ in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved $O_2$ concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for $O_2$ result in dissolved oxygen concentrations comparable to those in normal blood.




A Video Discussing Henry's Law. Video Link: Henry's Law (The Solubility of Gases in Solvents), YouTube(opens in new window) [youtu.be]

**Example 13.4.1**

The Henry's law constant for $O_2$ in water at 25°C is $1.27 \times 10^{-3} M/atm$, and the mole fraction of $O_2$ in the atmosphere is 0.21. Calculate the solubility of $O_2$ in water at 25°C at an atmospheric pressure of 1.00 atm.

**Given**: Henry's law constant, mole fraction of $O_2$, and pressure

**Asked for: solubility**

**Strategy**:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures)
B. Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

**Solution**:

A According to Dalton's law, the partial pressure of $O_2$ is proportional to the mole fraction of $O_2$:

$$\begin{aligned} P_A &= \chi_A P_t \\ &= (0.21)(1.00\ atm) \\ &= 0.21\ atm \end{aligned}$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$\begin{aligned} [CO_2] &= kP_{O_2} \\ &= (1.27 \times 10^{-3}\ M/\cancel{atm})(0.21\ \cancel{atm}) \\ &= 2.7 \times 10^{-4}\ M \end{aligned}$$

**Exercise 13.4.1**

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved $CO_2$ in a soft drink:

a. bottled under a pressure of 5.0 atm of $CO_2$
b. in equilibrium with the normal partial pressure of $CO_2$ in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry's law constant for $CO_2$ in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

**Answer a**

$0.17M$

**Answer b**

$1 \times 10^{-5}M$

## Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry's law describes the relationship between the pressure and the solubility of a gas.

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# 13.5: Colligative Properties of Solutions

**Learning Objectives**

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol (“antifreeze”) to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin colligatus, meaning “bound together” as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

**Counting concentrations**

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, $\mathrm{NaCl}$, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both $\mathrm{NaCl}$ and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of $\mathrm{NaCl}$ contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind.

## Vapor Pressure of Solutions and Raoult’s Law

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure 13.5.1, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

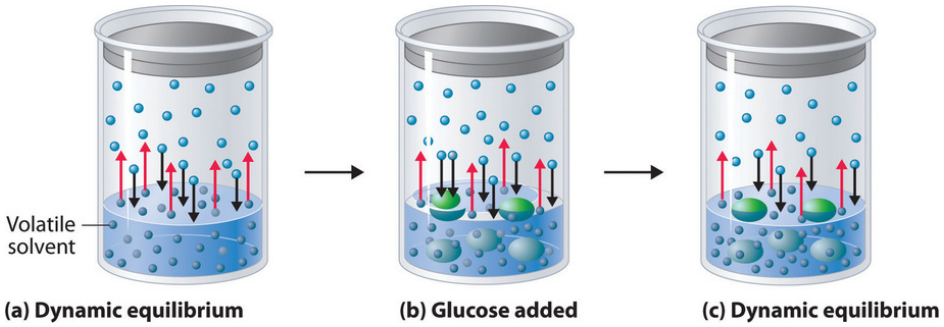



Figure 13.5.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water.

Figure 13.5.2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

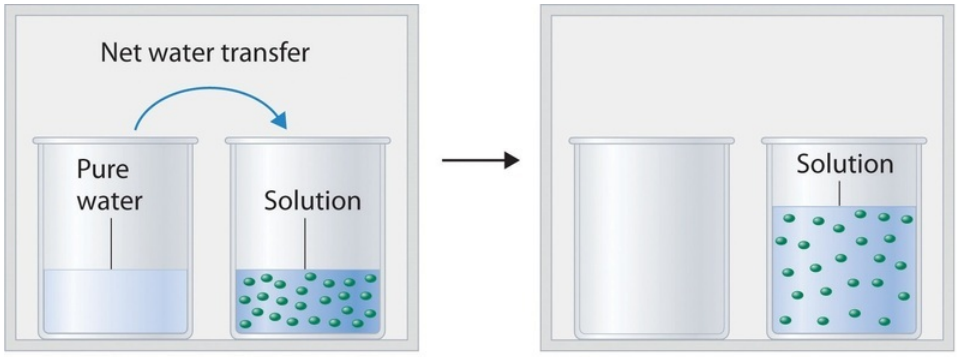



Figure 13.5.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution.

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = \chi_A P_A^0 \tag{13.5.1}$$

where $P_A$ is the vapor pressure of component A of the solution (in this case the solvent), $\chi_A$ is the mole fraction of $A$ in solution, and $P_A^0$ is the vapor pressure of pure $A$. Equation 13.5.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then $\chi_A + \chi_B = 1$, and we can substitute $\chi_A = 1 - \chi_B$ to obtain

$$P_A = (1 - \chi_B)P_A^0 \tag{13.5.2}$$

$$= P_A^0 - \chi_B P_A^0 \tag{13.5.3}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^0 - P_A = \Delta P_A \tag{13.5.4}$$

$$= \chi_B P_A^0 \tag{13.5.5}$$

We can solve vapor pressure problems in either of two ways: by using Equation 13.5.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 13.5.5 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

### Example 13.5.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

**Given**: identity of solute, percentage by mass, and vapor pressure of pure solvent

**Asked for**: vapor pressure of solution

**Strategy**:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law to calculate the vapor pressure of the solution.

**Solution**:

**A** A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g})\left(\frac{1\ mol}{62.07\ \cancel{g}}\right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g})\left(\frac{1\ mol}{18.02\ \cancel{g}}\right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

**B** From Raoult's law (Equation 13.5.1), the vapor pressure of the solution is

$$P_{H_2O} = (\chi_{H2_O})(P^0_{H_2O})$$
$$= (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 13.5.5 to calculate the resulting decrease in vapor pressure:

$$\chi_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} = 0.112$$

$$\Delta P_{H2_O} = (\chi_{EG})(P^0_{H_2O}) = (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{H_2O} = P^0_{H_2O} - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

**? Exercise 13.5.1**

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

**Answer**

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Even when a solute is volatile, meaning that it has a measurable vapor pressure, we can still use Raoult's law. In this case, we calculate the vapor pressure of each component separately. The total vapor pressure of the solution ($P_{tot}$) is the sum of the vapor pressures of the components:

$$P_{tot} = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0 \tag{13.5.6}$$

Because $\chi_B = 1 - \chi_A$ for a two-component system,

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0 \tag{13.5.7}$$

Thus we need to specify the mole fraction of only one of the components in a two-component system. Consider, for example, the vapor pressure of solutions of benzene and toluene of various compositions. At 20°C, the vapor pressures of pure benzene and toluene are 74.7 and 22.3 mmHg, respectively. The vapor pressure of benzene in a benzene–toluene solution is

$$P_{C_6H_6} = \chi_{C_6H_6} P^0_{C_6H_6} \tag{13.5.8}$$

and the vapor pressure of toluene in the solution is

$$PC_6H_5CH_3 = \chi_{C_6H_5CH_3} P^0_{C_6H_5CH3} \tag{13.5.9}$$

Equations 13.5.8 and 13.5.9 are both in the form of the equation for a straight line: $y = mx + b$, where $b = 0$. Plots of the vapor pressures of both components versus the mole fractions are therefore straight lines that pass through the origin, as shown in Figure 13.5.3. Furthermore, a plot of the total vapor pressure of the solution versus the mole fraction is a straight line that represents the sum of the vapor pressures of the pure components. Thus the vapor pressure of the solution is always greater than the vapor pressure of either component.

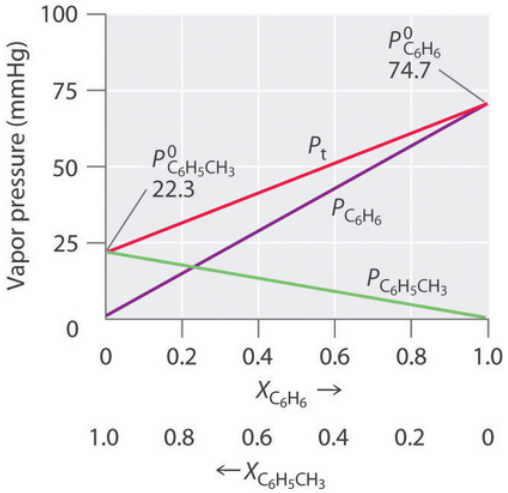



Figure 13.5.3: Vapor Pressures of Benzene–Toluene Solutions. Plots of the vapor pressures of benzene ($C_6H_6$) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution ($P_{tot}$) is the sum of the vapor pressures of the components.

Graph of vapp pressure in mmHg against benzene and toulen mole fractions. Benzene mole fractions increase from left to right while toluene mole fractions decrease from left to right on the x axis.

A solution of two volatile components that behaves like the solution in Figure 13.5.3, which is defined as a solution that obeys Raoult's law. Like an ideal gas, an ideal solution is a hypothetical system whose properties can be described in terms of a simple model. Mixtures of benzene and toluene approximate an ideal solution because the intermolecular forces in the two pure liquids are almost identical in both kind and magnitude. Consequently, the change in enthalpy on solution formation is essentially zero ($\Delta H_{soln} \approx 0$), which is one of the defining characteristics of an ideal solution.

> Ideal solutions and ideal gases are both simple models that ignore intermolecular interactions.

Most real solutions, however, do not obey Raoult's law precisely, just as most real gases do not obey the ideal gas law exactly. Real solutions generally deviate from Raoult's law because the intermolecular interactions between the two components A and B differ. We can distinguish between two general kinds of behavior, depending on whether the intermolecular interactions between molecules A and B are stronger or weaker than the A–A and B–B interactions in the pure components. If the A–B interactions are stronger than the A–A and B–B interactions, each component of the solution exhibits a lower vapor pressure than expected for an ideal solution, as does the solution as a whole. The favorable A–B interactions effectively stabilize the solution compared with the vapor. This kind of behavior is called a negative deviation from Raoult's law. Systems stabilized by hydrogen bonding between two molecules, such as acetone and ethanol, exhibit **negative deviations** from Raoult's law. Conversely, if the A–B interactions are weaker than the A–A and B–B interactions yet the entropy increase is enough to allow the solution to form, both A and B have an increased tendency to escape from the solution into the vapor phase. The result is a higher vapor pressure than expected for an ideal solution, producing a positive deviation from Raoult's law. In a solution of $CCl_4$ and methanol, for example, the nonpolar $CCl_4$ molecules interrupt the extensive hydrogen bonding network in methanol, and the lighter methanol molecules have weaker London dispersion forces than the heavier $CCl_4$ molecules. Consequently, solutions of $CCl_4$ and methanol exhibit **positive deviations** from Raoult's law.

### ✔ Example 13.5.2

For each system, compare the intermolecular interactions in the pure liquids and in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation).

a. cyclohexane and ethanol
b. methanol and acetone
c. n-hexane and isooctane (2,2,4-trimethylpentane)

**Given**: identity of pure liquids

**Asked for**: predicted deviation from Raoult's law (Equation 13.5.1)

**Strategy**:

Identify whether each liquid is polar or nonpolar, and then predict the type of intermolecular interactions that occur in solution.

**Solution**:

a. Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is nonpolar. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. Hence the A–B interactions will be weaker than the A–A and B–B interactions, leading to a higher vapor pressure than predicted by Raoult's law (a positive deviation).
b. Methanol contains an extensive hydrogen bonding network, but in this case the polar acetone molecules create A–B interactions that are stronger than the A–A or B–B interactions, leading to a negative enthalpy of solution and a lower vapor pressure than predicted by Raoult's law (a negative deviation).
c. Hexane and isooctane are both nonpolar molecules (isooctane actually has a very small dipole moment, but it is so small that it can be ignored). Hence the predominant intermolecular forces in both liquids are London dispersion forces. We expect the A–B interactions to be comparable in strength to the A–A and B–B interactions, leading to a vapor pressure in good agreement with that predicted by Raoult's law (an ideal solution).

**Exercise 13.5.2**

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation):

a. benzene and n-hexane
b. ethylene glycol and $CCl_4$
c. acetic acid and n-propanol

**Answer a**

approximately equal

**Answer b**

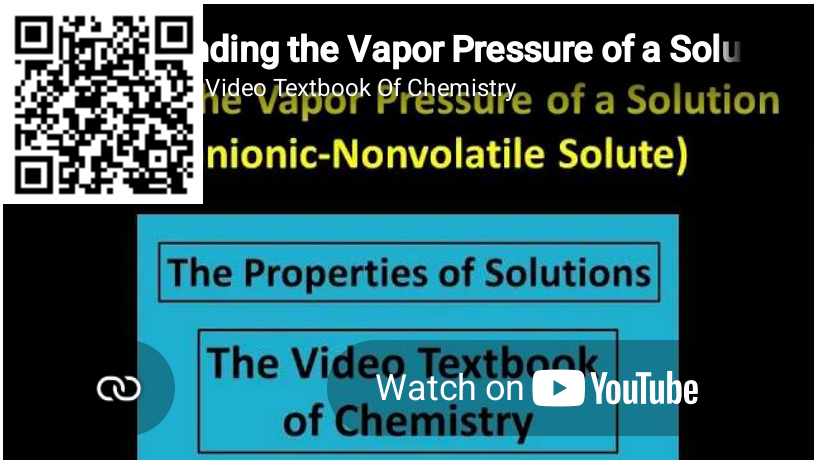
positive deviation (vapor pressure greater than predicted)

**Answer c**

negative deviation (vapor pressure less than predicted)




A Video Discussing Roult's Law. Video Link: Introduction to the Vapor Pressure of a Solution (Raoult's Law), YouTube(opens in new window) [youtu.be]




A Video Discussing How to find the Vapor Pressure of a Solution. Video Link: Finding the Vapor Pressure of a Solution (Nonionic-Nonvolatile Solute), YouTube(opens in new window) [youtu.be]

## Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 13.5.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to P = 1 atm at a higher temperature than does the curve for pure water.

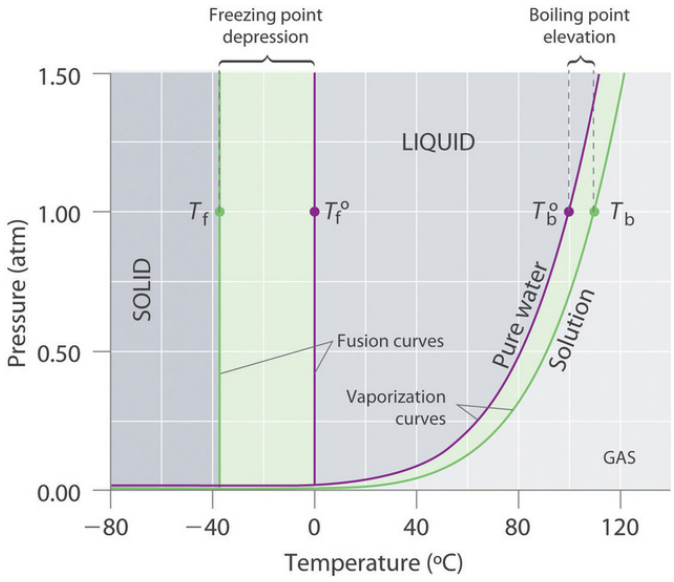



Figure 13.5.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.

> *The boiling point of a solution with a nonvolatile solute is **always** greater than the boiling point of the pure solvent.*

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 13.5.5).

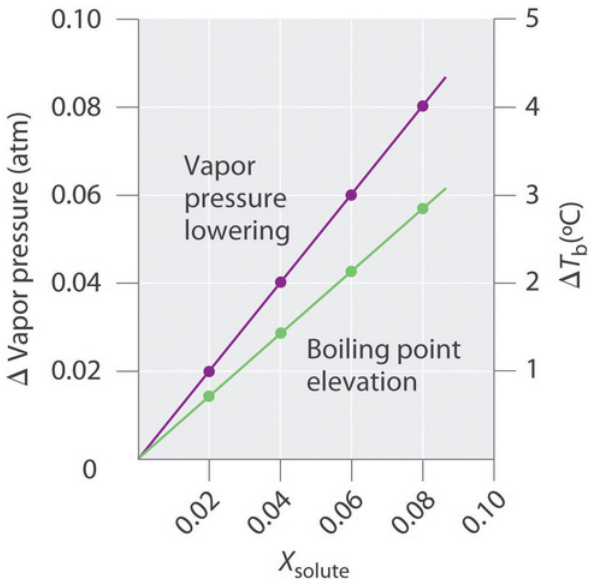



Figure 13.5.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute

Change in vapor pressure in atm in on the left side y axis while change in temperature is on the right side y axis. These are being plotted against mole fraction of solute.

We can define the boiling point elevation ($\Delta T_b$) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{13.5.10}$$

where $T_b$ is the boiling point of the solution and $T_b^0$ is the boiling point of the pure solvent. We can express the relationship between $\Delta T_b$ and concentration as follows

$$\Delta T_b = mK_b \tag{13.5.11}$$

where m is the concentration of the solute expressed in molality, and $K_b$ is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 13.5.1 lists characteristic $K_b$ values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 13.5.1: Boiling Point Elevation Constants ($K_b$) and Freezing Point Depression Constants ($K_f$) for Some Solvents

| Solvent | Boiling Point (°C) | $K_b$ (°C/m) | Freezing Point (°C) | $K_f$ (°C/m) |
|---|---|---|---|---|
| acetic acid | 117.90 | 3.22 | 16.64 | 3.63 |
| benzene | 80.09 | 2.64 | 5.49 | 5.07 |
| d-(+)-camphor | 207.4 | 4.91 | 178.8 | 37.8 |
| carbon disulfide | 46.2 | 2.42 | −112.1 | 3.74 |
| carbon tetrachloride | 76.8 | 5.26 | −22.62 | 31.4 |
| chloroform | 61.17 | 3.80 | −63.41 | 4.60 |
| nitrobenzene | 210.8 | 5.24 | 5.70 | 6.87 |
| water | 100.00 | 0.51 | 0.00 | 1.86 |

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 13.5.1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

### Example 13.5.3

In Example 13.5.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

**Given**: composition of solution

**Asked for**: boiling point

**Strategy**:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 13.5.11 to calculate the increase in boiling point.

**Solution**:

From Example 13.5.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.98\,m$$

From Equation 13.5.11, the increase in boiling point is therefore

$$\Delta T_b = mK_b = (6.98\,\cancel{m})(0.51°C/\cancel{m}) = 3.6°C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 13.5.11 may not be valid.

### Exercise 13.5.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

**Answer**

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)




A Video Discussing Boiling Point Elevation and Freezing Point Depression. Video Link: Boiling Point Elevation and Freezing Point Depression, YouTube(opens in new window) [youtu.be] (opens in new window)

## Freezing Point Depression

The phase diagram in Figure 13.5.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\ atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression ($\Delta T_f$) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{13.5.12}$$

where $T_f^0$ is the freezing point of the pure solvent and $T_f$ is the freezing point of the solution.

The order of the terms is reversed compared with Equation 13.5.10 to express the freezing point depression as a positive number. The relationship between $\Delta T_f$ and the solute concentration is given by an equation analogous to Equation 13.5.11:

$$\Delta T_f = mK_f \tag{13.5.13}$$

where $m$ is the molality of the solution and $K_f$ is the molal freezing point depression constant for the solvent (in units of °C/m).

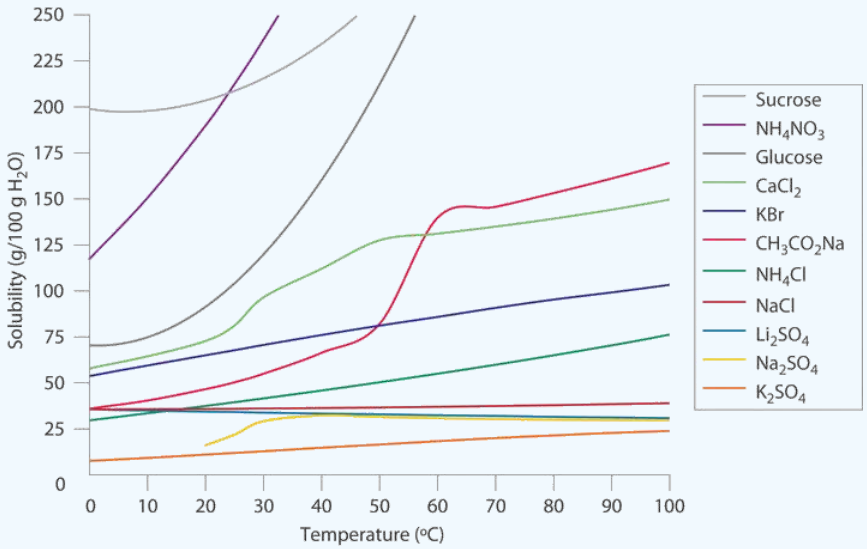
Like $K_b$, each solvent has a characteristic value of $K_f$ (see Table 13.5.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous $\mathrm{NaCl}$ solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

## Example 13.5.4: Salting the Roads

In colder regions of the United States, $NaCl$ or $CaCl_2$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of $NaCl$ and one of $CaCl_2$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.




Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, NaCl, Li2SO4, Na2SO4, K2SO4.

**Given**: solubilities of two compounds

**Asked for**: concentrations and freezing points

**Strategy**:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.

B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 13.5.13 to calculate the freezing point depressions of the solutions.

**Solution**:

A From Figure above, we can estimate the solubilities of $NaCl$ and $CaCl_2$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m$$

The lower formula mass of $NaCl$ more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $CaCl_2$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of $NaCl$ and $CaCl_2$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for

NaCl and 3 × 5.4 m = 16 m for $CaCl_2$. The resulting freezing point depressions can be calculated using Equation 13.5.13:

$$\text{NaCl}: \Delta T_f = mK_f = (12 \cancel{m})(1.86°C/\cancel{m}) = 22°C$$

$$\text{CaCl}_2: \Delta T_f = mK_f = (16 \cancel{m})(1.86°C/\cancel{m}) = 30°C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $CaCl_2$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $CaCl_2$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

**? Exercise 13.5.4**

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 13.5.5 and 13.5.5.

**Answer**

−13.0°C

**✓ Example 13.5.5**

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m $KCl$, 0.1 m glucose, 0.1 m SrCl2, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

**Given**: molalities of six solutions

**Asked for:** relative freezing points

**Strategy**:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.
B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

**Solution**:

**A** Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $SrCl_2$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

**B** The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $SrCl_2$.

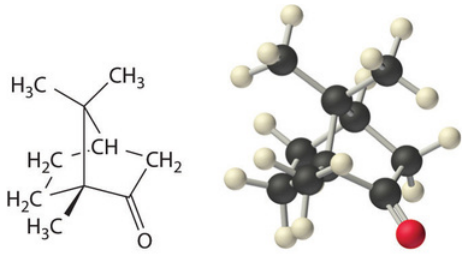
**? Exercise 13.5.5**

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $CaCl_2$, and 0.2 m sucrose.

**Answer**

0.2 m $\mathrm{NaCl}$ (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $\mathrm{CaCl_2}$ < 0.2 m sucrose (highest freezing point)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing $K_b$ and $K_f$ values in Table 13.5.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of $K_f$ (37.8°C/m), d-(+)-camphor (Table 13.5.1) is often used to determine the molar mass of organic compounds by this method.




*d*-(+)-Camphor

## Example 13.5.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of $CS_2$ to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved $\mathrm{S}_n$ molecules (i.e., what is the value of $n$?).

**Given**: masses of solute and solvent and freezing point

**Asked for**: molar mass and number of $\mathrm{S}$ atoms per molecule

**Strategy**:

A. Use Equation 13.5.12, the measured freezing point of the solution, and the freezing point of $CS_2$ from Table 13.5.1 to calculate the freezing point depression. Then use Equation 13.5.13 and the value of $K_f$ from Table 13.5.1 to calculate the molality of the solution.
B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain $n$, the number of sulfur atoms per mole of dissolved sulfur.

**Solution**:

A The first step is to calculate the freezing point depression using Equation 13.5.12:

$$\Delta T_f = T_f^0 - T_f = -112.1°C - (-113.5°C) = 1.4°C$$

Then Equation 13.5.13 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4°\cancel{C}}{3.74°\cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

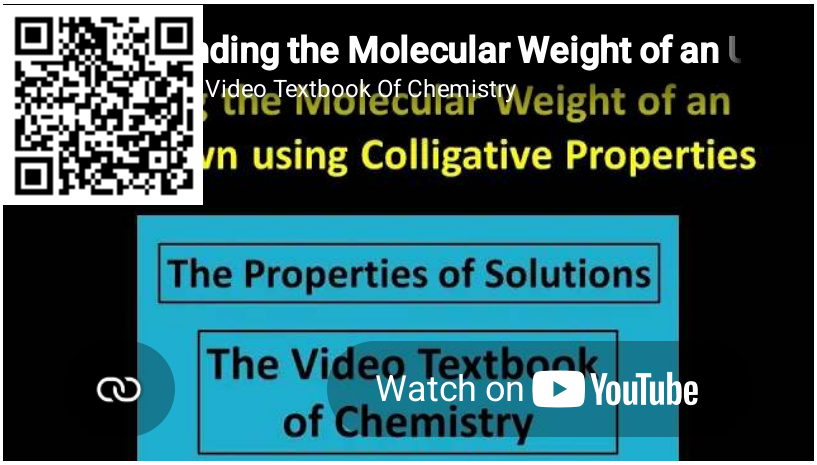
The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of $S_8$.

**? Exercise 13.5.6**

One of the byproducts formed during the synthesis of $C_{60}$ is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of $CCl_4$ has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

**Answer**

847 g/mol; $C_{70}$




A Video Discussing how to find the Molecular Weight of an Unknown using Colligative Properties. Video Link: Finding the Molecular Weight of an Unknown using Colligative Properties, YouTube(opens in new window) [youtu.be]

## Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 13.5.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

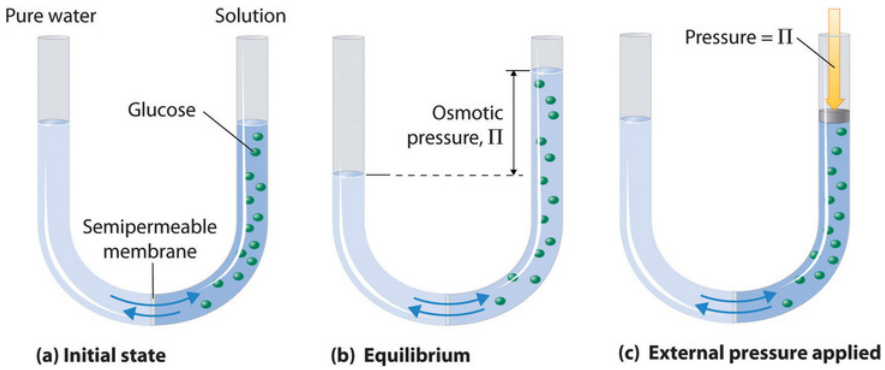



Figure 13.5.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution ( $\Pi_{soln}$), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{13.5.14}$$

where $M$ is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), $R$ is the ideal gas constant, and $T$ is the absolute temperature.

As shown in Example 13.5.7, osmotic pressures tend to be quite high, even for rather dilute solutions.

### Example 13.5.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

**Given**: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

**Asked for**: osmotic pressure of NaCl solution and concentration of glycerol needed

**Strategy**:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 13.5.14 to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 13.5.14 to calculate the molarity of glycerol needed to create this osmotic pressure.

**Solution**:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$M_{NaCl} = \frac{moles\ NaCl}{\text{liter solution}}$$
$$= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right)$$
$$= 0.70\ M\ \text{NaCl}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 13.5.14 to calculate the osmotic pressure of the solution:

$$\Pi = MRT$$
$$= (1.4\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K)$$
$$= 34\ atm$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 13.5.14 for the molarity corresponding to this osmotic pressure:

$$M = \frac{\Pi}{RT}$$
$$= \frac{27\ \cancel{atm}}{[0.0821(L \cdot \cancel{atm})/(\cancel{K} \cdot mol)](298\ \cancel{K})}$$
$$= 1.1\ M\ \text{glycerol}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

**? Exercise 13.5.7**

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

**Answer**

24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 13.5.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

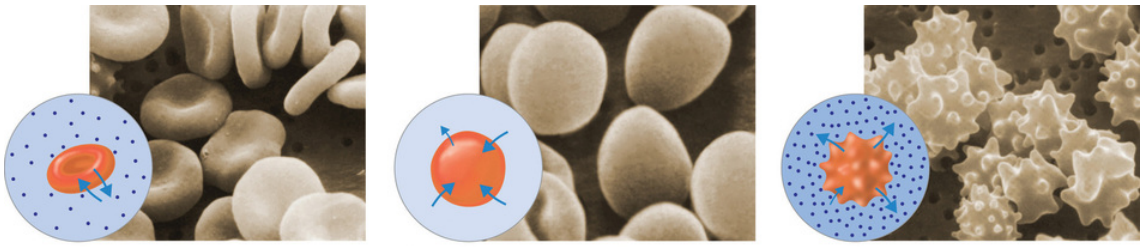



Figure 13.5.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 13.5.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

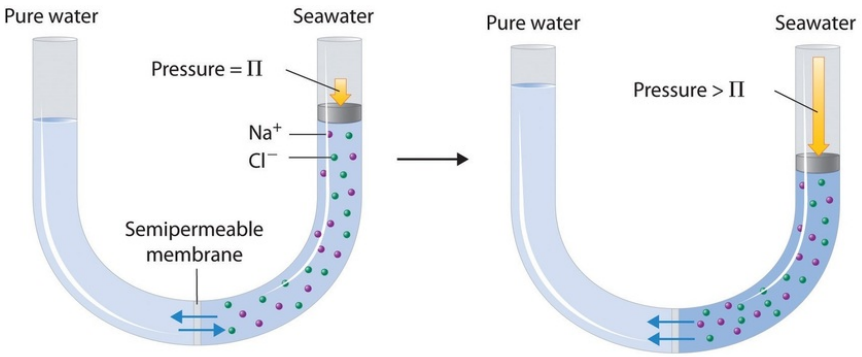
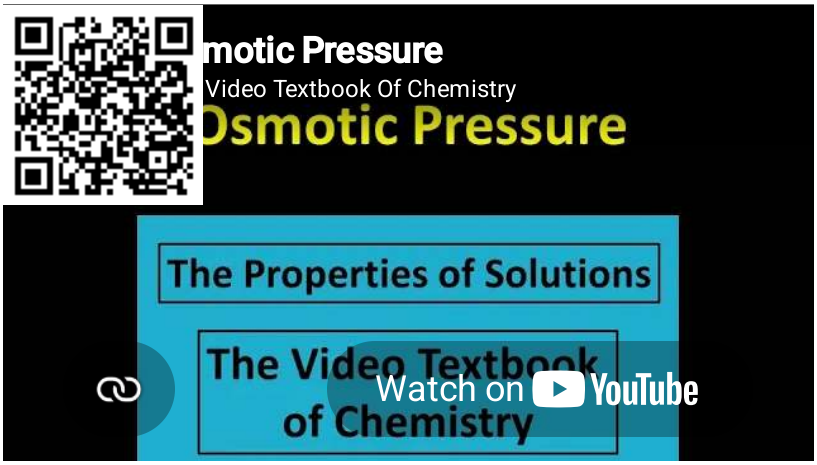



Figure 13.5.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure ($\Pi_{soln}$), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.




A Video Discussing Osmotic Pressure. Video Link: Osmotic Pressure, YouTube(opens in new window) [youtu.be] (opens in new window)

## Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of $\mathrm{NaCl}$ in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of $\mathrm{NaCl}$ and $\mathrm{KCl}$ are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van't Hoff factor ($i$) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{13.5.15}$$

Named for Jacobus Hendricus van't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

> *As the solute concentration increases, the van't Hoff factor decreases.*

The van't Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van't Hoff factor, the greater the deviation. As the data in Table 13.5.2 show, the van't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table 13.5.2: van't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

| Compound | i (measured) | i (ideal) |
|---|---|---|
| glucose | 1.0 | 1.0 |
| sucrose | 1.0 | 1.0 |
| $NaCl$ | 1.9 | 2.0 |
| $HCl$ | 1.9 | 2.0 |
| $MgCl_2$ | 2.7 | 3.0 |
| $FeCl_3$ | 3.4 | 4.0 |
| $Ca(NO_3)_2$ | 2.5 | 3.0 |
| $AlCl_3$ | 3.2 | 4.0 |
| $MgSO_4$ | 1.4 | 2.0 |

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 13.5.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as $Mg^{2+}$, $Al^{3+}$, $SO_4^{2-}$, and $PO_4^{3-}$ have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

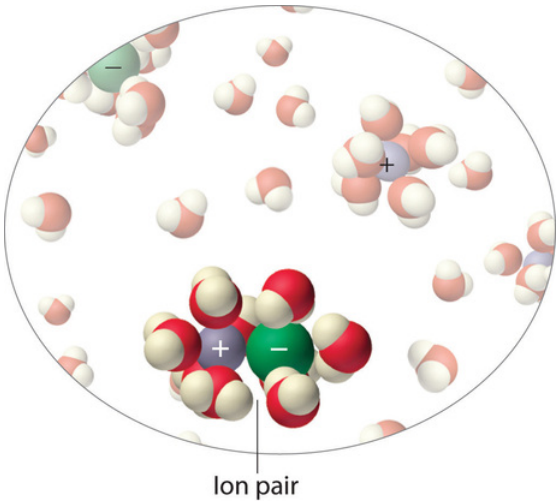



Figure 13.5.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

### Example 13.5.8: Iron Chloride in Water

A 0.0500 M aqueous solution of $FeCl_3$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van't Hoff factor $i$ for the solution.

**Given**: solute concentration, osmotic pressure, and temperature

**Asked for**: van't Hoff factor

**Strategy**:

A. Use Equation 13.5.14 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.

B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 13.5.15 to calculate the van't Hoff factor.

**Solution**:

A If $FeCl_3$ dissociated completely in aqueous solution, it would produce four ions per formula unit [Fe3+(aq) plus 3Cl−(aq)] for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\begin{aligned}\Pi &= MRT \\ &= (0.200\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) = 4.89\ atm\end{aligned}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 particles per mole of $FeCl_3$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\left(\frac{0.0821\ (L \cdot atm)}{(K \cdot mol)}\right)(298\ K)$$

or after rearranging

$$M = 0.170 mol$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 particles per mole of $FeCl_3$ dissolved. From Equation 13.5.15, the van't Hoff factor for the solution is

$$i = \frac{3.40 \text{ particles observed}}{1 \text{ formula unit } FeCl_3} = 3.40$$

**? Exercise 13.5.8: Magnesium Chloride in Water**

Calculate the van't Hoff factor for a 0.050 m aqueous solution of $MgCl_2$ that has a measured freezing point of −0.25°C.

**Answer**

2.7 (versus an ideal value of 3).




A Video Discussing the Colligative Properties in Solutions. Video Link: Colligative Properties in Solutions, YouTube(opens in new window) [youtu.be]

## Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law. The boiling

point elevation ($\Delta T_b$) and freezing point depression ($\Delta T_f$) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form ion pairs, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the van't Hoff factor (i), the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = \chi_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = \chi_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0$$

- **boiling point elevation**:

$$\Delta T_b = mK_b$$

- **freezing point depression:**

$$\Delta T_f = mK_f$$

- **osmotic pressure**:

$$\Pi = nRTV = MRT$$

- **van 't Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

---

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# 13.6: Aggregate Particles

**Learning Objectives**

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspensionA heterogeneous mixture of particles with diameters of about 1 µm that are distributed throughout a second phase and that separate from the dispersing phase on standing. is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloidA heterogeneous mixture of particles with diameters of about 2–500 nm that are distributed throughout a second phase and do not separate from the dispersing phase on standing. is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 13.6.1.

Table 13.6.1 Properties of Liquid Solutions, Colloids, and Suspensions

| Type of Mixture | Approximate Size of Particles (nm) | Characteristic Properties | Examples |
|---|---|---|---|
| solution | < 2 | not filterable; does not separate on standing; does not scatter visible light | air, white wine, gasoline, salt water |
| colloid | 2–500 | scatters visible light; translucent or opaque; not filterable; does not separate on standing | smoke, fog, ink, milk, butter, cheese |
| suspension | 500–1000 | cloudy or opaque; filterable; separates on standing | muddy water, hot cocoa, blood, paint |

## Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word *colloid* (from the Greek *kólla*, meaning "glue") to describe these substances, as well as the words solA dispersion of solid particles in a liquid or solid. and gelA semisolid sol in which all of the liquid phase has been absorbed by the solid particles. to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosolsA dispersion of solid or liquid particles in a gas., which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effectThe phenomenon of scattering a beam of visible light.,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen

from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 13.6.1



**Figure 13.6.1 Tyndall Effect, the Scattering of Light by Colloids** The glass on the left has dilute colloidal silver, the one on the right tap water. The red laser pointer beam is scattered by the Tyndall effect in the glass on the left.

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called *albumin*, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a "donut" shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine, Figure 9.7.1 5.16). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 13.6.2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with "normal" hemoglobin.

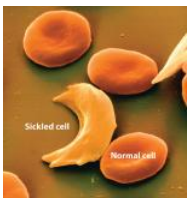



**Figure 13.6.2 Sickle-Cell Anemia** The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.

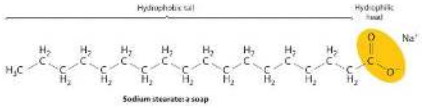


**Figure 13.6.3 Formation of New Land by the Destabilization of a Colloid Suspension** This satellite photograph shows the Mississippi River delta from New Orleans (*top*) to the Gulf of Mexico (*bottom*). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (*tan area*).

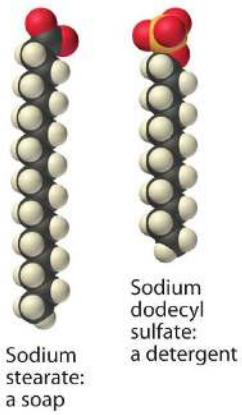
Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 13.6.3. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

## Emulsions

EmulsionsA dispersion of one liquid phase in another liquid with which it is immiscible. are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic "tail" with a hydrophilic "head":



Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate [$CH_3(CH_2)_{16}CO_2^-Na^+$], and detergents, such as sodium dodecyl sulfate [$CH_3(CH_2)_{11}OSO_3^-Na^+$], whose structures are as follows:




When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called *bile* into the small intestine. Bile contains a variety of *bile salts*, detergent-like molecules that emulsify the fats.

## Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micellesA spherical or cylindrical aggregate of detergents or soaps in water that minimizes contact between the hydrophobic tails of the detergents or soaps and water., which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (part (a) in Figure 13.6.4).

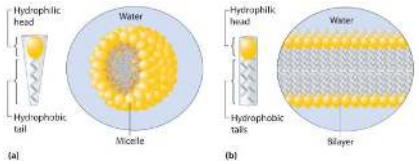



Figure 13.6.4 Micelles and a Phospholipid Bilayer (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipidsA large class of biological, detergent-like molecules that have a hydrophilic head and two hydrophobic tails and that form bilayers. consists of detergent-like molecules with a hydrophilic head and *two* hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayersA two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail., extended sheets consisting of a double layer of molecules. As shown in part (b) in Figure 13.6.4, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.




A cell membraneA mixture of phospholipids that form a phospholipid bilayer around the cell. is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cellA collection of molecules, capable of reproducing itself, that is surrounded by a phospholipid bilayer. is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

## Summary

A **suspension** is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a **colloid** are smaller and do not separate on standing. A colloid can be classified as a **sol**, a dispersion of solid particles in a liquid or solid; a **gel**, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an **aerosol**, a dispersion of solid or liquid particles in a gas; or an **emulsion**, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the **Tyndall effect**. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. **Emulsions** are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called **micelles**. **Phospholipids** are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A **bilayer** is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. **Cells** are collections of molecules that are surrounded by a phospholipid bilayer called a **cell membrane** and are able to reproduce themselves.

## Key Takeaway

- Colloids and suspensions are mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures.

## Conceptual Problems

1. How does a colloid differ from a suspension? Which has a greater effect on solvent properties, such as vapor pressure?
2. Is homogenized milk a colloid or a suspension? Is human plasma a colloid or a suspension? Justify your answers.

3. How would you separate the components of an emulsion of fat dispersed in an aqueous solution of sodium chloride?

## Contributors

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# 13.7: Aggregate Particles in Aqueous Solution

**Learning Objectives**

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 13.9.

**Table 13.9** Properties of Liquid Solutions, Colloids, and Suspensions

| Type of Mixture | Approximate Size of Particles (nm) | Characteristic Properties | Examples |
|---|---|---|---|
| solution | < 2 | not filterable; does not separate on standing; does not scatter visible light | air, white wine, gasoline, salt water |
| colloid | 2–500 | scatters visible light; translucent or opaque; not filterable; does not separate on standing | smoke, fog, ink, milk, butter, cheese |
| suspension | 500–1000 | cloudy or opaque; filterable; separates on standing | muddy water, hot cocoa, blood, paint |

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# CHAPTER OVERVIEW

## 14: Chemical Kinetics


14.1: Preview to Chemical Equilibria
14.2: Factors that Affect Reaction Rates
14.3: Reaction Rates and Rate Laws
14.4: Methods of Determining Reaction Order
14.5: Using Graphs to Determine Rate Laws, Rate Constants and Reaction Orders
14.6: Half Lives and Radioactive Decay Kinetics
14.7: Reaction Rates - A Microscopic View
14.8: The Collision Model of Chemical Kinetics
14.9: Catalysis


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## 14.1: Preview to Chemical Equilibria

In Chapter 14, we discussed the principles of chemical kinetics, which deal with the rate of change, or how quickly a given chemical reaction occurs. We now turn our attention to the extent to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are reversible to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches chemical equilibrium, the point at which the composition of the system no longer changes with time.



*A smoggy sunset in Shenzhen, China. The reaction of $O_2$ with $N_2$ at high temperature in an internal combustion engine produces small amounts of $NO$, which reacts with atmospheric $O_2$ to form $NO_2$, an important component of smog. The reddish-brown color of $NO_2$ is responsible for the characteristic color of smog, as shown in this true-color photo.*

We introduced the concept of equilibrium in Chapter 11, where you learned that a liquid and a vapor are in equilibrium when the number of molecules evaporating from the surface of the liquid per unit time is the same as the number of molecules condensing from the vapor phase. Vapor pressure is an example of a physical equilibrium because only the physical form of the substance changes. Similarly, in Chapter 13, we discussed saturated solutions, another example of a physical equilibrium, in which the rate of dissolution of a solute is the same as the rate at which it crystallizes from solution.

In this chapter, we describe the methods chemists use to quantitatively describe the composition of chemical systems at equilibrium, and we discuss how factors such as temperature and pressure influence the equilibrium composition. As you study these concepts, you will also learn how urban smog forms and how reaction conditions can be altered to produce $H_2$ rather than the combustion products $CO_2$ and $H_2O$ from the methane in natural gas. You will discover how to control the composition of the gases emitted in automobile exhaust and how synthetic polymers such as the polyacrylonitrile used in sweaters and carpets are produced on an industrial scale.

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# 14.2: Factors that Affect Reaction Rates

**Learning Objectives**

- To understand the factors that affect reaction rates.

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either are present. By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

## Concentration Effects

Two substances cannot possibly react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more reactant particles that collide per unit time, the more often a reaction between them can occur. Consequently, the reaction rate usually increases as the concentration of the reactants increases. One example of this effect is the reaction of sucrose (table sugar) with sulfuric acid, which is shown in Figure 14.1.1.





**Figure 14.1.1 The Effect of Concentration on Reaction Rates** Mixing sucrose with *dilute* sulfuric acid in a beaker (a, right) produces a simple solution. Mixing the same amount of sucrose with *concentrated* sulfuric acid (a, left) results in a dramatic reaction (b) that eventually produces a column of black porous graphite (c) and an intense smell of burning sugar.

## Temperature Effects

You learned in Chapter 10 that increasing the temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster, so they collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate of virtually all reactions decreases with decreasing temperature. For example, refrigeration retards the rate of growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce. Figure 14.1.2 shows how temperature affects the light emitted by two chemiluminescent light sticks.





**Figure 14.1.2 The Effect of Temperature on Reaction Rates**At **high** temperature, the reaction that produces light in a chemiluminescent light stick occurs more rapidly, producing more photons of light per unit time. Consequently, the light glows brighter in hot water (left) than in ice water (right).

In systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100°C, ethanol is converted to diethyl ether:

$$2CH_3CH_2OH \overset{H_2SO_4}{\longrightarrow} CH_3CH_2OCH_2CH_3 + H_2O$$

At 180°C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$CH_3CH_2OH \overset{H_2SO_4}{\longrightarrow} CH_2CH_2 + H_2O$$

## Phase and Surface Area Effects

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

Automobile engines use surface area effects to increase reaction rates. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction (Figure 14.1.3 ). Similar phenomena are partially responsible for dust explosions that occasionally destroy grain elevators or coal mines.






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# 14.3: Reaction Rates and Rate Laws

**Learning Objectives**

- To determine the reaction rate.
- To understand the meaning of a rate law.

The factors discussed in Section 14.1 affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

## Reaction Rates

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the *change* in the concentration per unit time.

The progress of a simple reaction (A → B) is shown in Figure 14.2.1 where the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 14.2.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

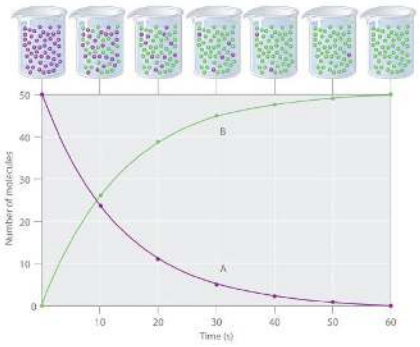



Figure 14.2.1 The Progress of a Simple Reaction (A → B) The mixture initially contains only A molecules (purple). With increasing time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

$$rate = \frac{\Delta [B]}{\Delta t} = -\frac{\Delta [A]}{\Delta t}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δ*t* to convert that expression to a positive number. The reaction rate we would calculate for the reaction A → B using Equation 14.2.1 would be different for each interval. (This is not true for every reaction, as you will see later.) A much greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, which means that the reaction rate is fastest at first. This is consistent with the concentration effects described in Section 14.1because the concentration of A is greatest at the beginning of the reaction.

### Note the Pattern

Reaction rates generally decrease with time as reactant concentrations decrease.

## Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 14.2.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world. (More than 25,000,000 kg are produced annually worldwide.) Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid.

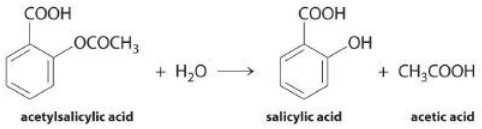



**Figure 14.2.2** Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 14.2.1 and are shown in the graph in Figure 14.2.3. These data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

**Table 14.2.1 Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C***

| Time (h) | [Aspirin] (M) | [Salicylic Acid] (M) |
|---|---|---|
| 0 | $5.55 \times 10^{-3}$ | 0 |
| 2.0 | $5.51 \times 10^{-3}$ | $0.040 \times 10^{-3}$ |
| 5.0 | $5.45 \times 10^{-3}$ | $0.10 \times 10^{-3}$ |
| 10 | $5.35 \times 10^{-3}$ | $0.20 \times 10^{-3}$ |
| 20 | $5.15 \times 10^{-3}$ | $0.40 \times 10^{-3}$ |
| 30 | $4.96 \times 10^{-3}$ | $0.59 \times 10^{-3}$ |
| 40 | $4.78 \times 10^{-3}$ | $0.77 \times 10^{-3}$ |
| 50 | $4.61 \times 10^{-3}$ | $0.94 \times 10^{-3}$ |
| 100 | $3.83 \times 10^{-3}$ | $1.72 \times 10^{-3}$ |
| 200 | $2.64 \times 10^{-3}$ | $2.91 \times 10^{-3}$ |
| 300 | $1.82 \times 10^{-3}$ | $3.73 \times 10^{-3}$ |

*The reaction at pH 7.0 is very slow. It is *much* faster under acidic conditions, such as those found in the stomach.

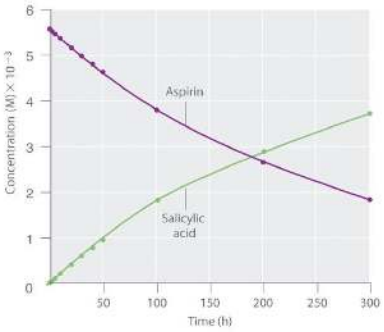



Figure 14.2.3 The Hydrolysis of **Aspirin**This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.2.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

We can calculate the average reaction rateThe reaction rate calculated for a given time interval from the concentrations of either the reactant or one of the products at the beginning of the interval time

$$rate_{(t=0-2.0\ h)} = \frac{[salicylic\ acid]_2 - [salicylic\ acid]_0}{2.0\ h - 0.0\ h}$$

$$= \frac{0.040 \times 10^{-3}\ M - 0.000\ M}{2.0\ h - 0.0\ h} = 2 \times 10^{-5}\ M/h$$


https://chem.libretexts.org/@go/page/349739

We can also calculate the reaction rate from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$rate_{(t=0-2.0\ h)} = \frac{[aspirin]_2 - [aspirin]_0}{2.0\ h - 0.0\ h}$$

$$rate_{(t=0-2.0\ h)} = \frac{5.51 \times 10^{-3}\ M - 5.55 \times 10^{-3}\ M}{2.0\ h - 0.0\ h} = 2.0 \times 10^{-5}\ M/h\backslash;\text{h}\}\ \backslash)$$

If we now calculate the reaction rate during the last interval given in Table 14.2.1 (the interval between 200 h and 300 h after the start of the reaction), we find that the reaction rate is significantly slower than it was during the first interval ($t$ = 0–2.0 h):

$$rate_{(t=200-300\ h)} = \frac{[salicylic\ acid]_{300} - [salicylic\ acid]_{200}}{300\ h - 200\ h}$$

$$= \frac{3.73 \times 10^{-3}\ M - 2.91 \times 10^{-3}\ M}{100;h} = 8.2 \times 10^{-6}\ M/h$$

(You should verify from the data in Table 14.2.1 that you get the same rate using the concentrations of aspirin measured at 200 h and 300 h.)

## Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Let us look at a reaction in which the coefficients are *not* all the same: the fermentation of sucrose to ethanol and carbon dioxide, which we encountered in Chapter 8

$$\underset{sucrose}{C_{12}H_{22}O_{11}\,(aq)} + H_2O\,(l) \rightarrow 4C_2H_5OH\,(aq) + CO_2\,(g)$$

The coefficients show us that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, we can find the reaction rate by looking at the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as you learned in Chapter 10, the volume of $CO_2$ gas formed will depend on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$rate = \frac{\Delta\,[C_2H_5OH]}{\Delta t} = -\frac{4\Delta\,[sucrose])}{\Delta t}$$

The concentration of the reactant—in this case sucrose—*decreases* with increasing time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 14.2.3 so that the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with increasing time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product that has the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 14.2.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$rate = -\frac{\Delta\,[sucrose]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta\,[C_2H_5OH]}{\Delta t}\right)$$

### Example 14.2.1

Consider the thermal decomposition of gaseous $N_2O_5$ to $NO_2$ and $O_2$ via the following equation:

$$2N_2O_5\,(g) \overset{\Delta}{\rightarrow} 4NO_2\,(g) + O_2\,(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

**Given:** balanced chemical equation

**Asked for:** reaction rate expressions

**Strategy:**

**A** Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.

**B** For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

**Solution:**

**A** Because $O_2$ has the smallest coefficient in the balanced chemical equation for the reaction, we define the reaction rate as the rate of change in the concentration of $O_2$ and write that expression.

**B** We know from the balanced chemical equation that 2 mol of $N_2O_5$ must decompose for each 1 mol of $O_2$ produced and that 4 mol of $NO_2$ are produced for every 1 mol of $O_2$ produced. The molar ratios of $O_2$ to $N_2O_5$ and to $NO_2$ are thus 1:2 and 1:4, respectively. This means that we divide the rate of change of $[N_2O_5]$ and $[NO_2]$ by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because $NO_2$ is produced at four times the rate of $O_2$, we must divide the rate of production of $NO_2$ by 4. The reaction rate expressions are as follows:

$$rate = \frac{\Delta\left[O_2\right]}{\Delta t} = \frac{\Delta\left[NO_2\right]}{4\Delta t} = -\frac{\Delta\left[N_2O_5\right]}{2\Delta t}$$

Exercise

The key step in the industrial production of sulfuric acid is the reaction of $SO_2$ with $O_2$ to produce $SO_3$.

$$2SO_2\left(g\right) + O_2\left(g\right) \rightarrow 2SO_3\left(g\right)$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

**Answer**

$$rate = -\frac{\Delta\left[O_2\right]}{\Delta t} = -\frac{\Delta\left[SO_2\right]}{\Delta t} = \frac{\Delta\left[SO_3\right]}{2\Delta t}$$

### Example 14.2.2

Using the reaction shown in Example 1, calculate the reaction rate from the following data taken at 56°C:

| | | | $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ |
|---|---|---|---|
| Time (s) | $[N_2O_5]$ (M) | $[NO_2]$ (M) | $[O_2]$ (M) |
| 240 | 0.0388 | 0.0314 | 0.00792 |
| 600 | 0.0197 | 0.0699 | 0.0175 |

**Given:** balanced chemical equation and concentrations at specific times

**Asked for:** reaction rate

**Strategy:**

**A** Using the equations in Example 1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

**B** Substitute the value for the time interval into the equation. Make sure your units are consistent.

**Solution:**

**A** We are asked to calculate the reaction rate in the interval between $t_1$ = 240 s and $t_2$ = 600 s. From Example 1, we see that we can evaluate the reaction rate using any of three expressions:

$$rate = \frac{\Delta\left[O_2\right]}{\Delta t} = \frac{\Delta\left[NO_2\right]}{4\Delta t} = -\frac{\Delta\left[N_2O_5\right]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of $N_2O_5$ and inserting the corresponding time interval into the rate expression for $N_2O_5$,

$$rate = -\frac{\Delta\left[N_2O_5\right]}{2\Delta t} = -\frac{\left[N_2O_5\right]_{600} - \left[N_2O_5\right]_{240}}{2\left(600\ s - 240\ s\right)}$$

**B** Substituting actual values into the expression,

$$rate = -\frac{0.197\ M - 0.0388\ M}{2\,(360\ s)}$$

Similarly, we can use $NO_2$ to calculate the reaction rate:

$$rate = -\frac{\Delta\,[NO_2]}{4\Delta t} = -\frac{[NO_2]_{600} - [NO_2]_{240}}{4\,(600\ s - 240\ s)} = \frac{0.0699\ M - 0.0314\ M}{4\,(360)} = 2.67 \times 10^{-5}\ M/s$$

If we allow for experimental error, this is the same rate we obtained using the data for $N_2O_5$, as it should be because the reaction rate should be the same no matter which concentration is used. We can also use the data for $O_2$:

$$rate = -\frac{\Delta\,[O_2]}{\Delta t} = -\frac{[O_2]_{600} - [O_2]_{240}}{(600\ s - 240\ s)} = \frac{0.0175\ M - 0.00792\ M}{360\ s} = 2.66 \times 10^{-5}\ M/s$$

Again, this is the same value we obtained from the $N_2O_5$ and $NO_2$ data. Thus the reaction rate does not depend on which reactant or product is used to measure it.

Exercise

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

| | | | $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ |
|---|---|---|---|
| Time (s) | $[SO_2]$ (M) | $[O_2]$ (M) | $[SO_3]$ (M) |
| 300 | 0.0270 | 0.0500 | 0.0072 |
| 720 | 0.0194 | 0.0462 | 0.0148 |

**Answer:** $9.0 \times 10^{-6}$ M/s

## Instantaneous Rates of Reaction

So far, we have determined average reaction rates over particular intervals of time. We can also determine the instantaneous rateThe reaction rate of a chemical reaction at any given point in time. of a reaction, which is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate.If you have studied calculus, you may recognize that the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

Think of the distinction between the instantaneous and average rates of a reaction as being similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although you may travel for a long time at 65 mph on an interstate highway during a long trip, there may be times when you travel only 25 mph in construction zones or 0 mph if you stop for meals or gas. Thus your average speed on the trip may be only 50 mph, whereas your instantaneous speed on the interstate at a given moment may be 65 mph. Whether you are able to stop the car in time to avoid an accident depends on your instantaneous speed, not your average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval normally has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

In chemical kinetics, we generally focus on one particular instantaneous rate, which is the initial reaction rate, $t = 0$. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to $t = 0$.

## Rate Laws

In Section 14.1, you learned that reaction rates generally decrease with time because reactant concentrations decrease as reactants are converted to products. You also learned that reaction rates generally increase when reactant concentrations are increased. We now examine the mathematical expressions called rate lawsMathematical expressions that describe the relationships between reactant rates and reactant concentrations in a chemical reaction., which describe the relationships between reactant rates and

reactant concentrations. Rate laws are laws as defined in Chapter 1; that is, they are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A differential rate lawA rate law that expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt) expresses the reaction rate in terms of *changes* in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δ*t*). In contrast, an integrated rate lawA rate law that expresses the reaction rate in terms of the initial concentration $[R]_0$ and the measured concentration of one or more reactants ([R]) after a given amount of time (t) describes the reaction rate in terms of the *initial* concentration ($[R]_0$) and the *measured* concentration of one or more reactants ([R]) after a given amount of time (*t*); we will discuss integrated rate laws in Section 14.3. The integrated rate law can be found by using calculus to integrate the differential rate law, although the method of doing so is beyond the scope of this text. *Whether you use a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).*

## Reaction Orders

For a reaction with the general equation

$$aA + bB \rightarrow cC + dD$$

the experimentally determined rate law usually has the following form:

$$rate = k\,[A]^m\,[B]^n$$

The *proportionality constant* (*k*) is called the rate constantA proportionality constant whose value is characteristic of the reaction and the reaction conditions and whose numerical value does not change as the reaction progresses under a given set of conditions., and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular value of the rate constant under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of *k*, however, does *not* change as the reaction progresses under a given set of conditions.

Thus the reaction rate depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers *m* and *n*, respectively. The values of *m* and *n* are derived from experimental measurements of the changes in reactant concentrations over time and indicate the reaction orderNumbers that indicate the degree to which the reaction rate depends on the concentration of each reactant., the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers. For example, Equation 14.2.6 tells us that Equation 14.2.5 is *m*th order in reactant A and *n*th order in reactant B. It is important to remember that *n* and *m* are not related to the stoichiometric coefficients *a* and *b* in the balanced chemical equation and must be determined experimentally. The *overall reaction order* is the sum of all the exponents in the rate law: *m* + *n*.

### Note the Pattern

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

Although differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, integrated rate laws are used to determine the reaction order and the value of the rate constant from experimental measurements. (We present general forms for integrated rate laws in Section 14.3.) To illustrate how chemists interpret a differential rate law, we turn to the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone. This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3\,CBr\,(soln) + H_2O\,(soln) \rightarrow (CH_3)_3\,COH\,(soln) + HBr\,(soln)$$

Combining the rate expression in Equation 14.4 and Equation 14.9 gives us a general expression for the differential rate law:

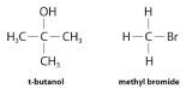
$$rate = -\frac{\Delta\,[A]}{\Delta t} = k\,[A]^m\,[B]^n$$

Inserting the identities of the reactants into Equation 14.2.8 gives the following expression for the differential rate law for the reaction:

$$rate = -\frac{\Delta\,[(CH_3)_3\,CBr]}{\Delta t} = k\,[(CH_3)_3\,CBr]^m\,[H_2O]^n$$

Experiments done to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Thus *m* and *n* in Equation 14.12 are 1 and 0, respectively, and

$$rate = k\left[(CH_3)_3 CBr\right]^1 \left[H_2O\right]^0 = k\left[(CH_3)_3 CBr\right]$$




Because the exponent for the reactant is 1, the reaction is *first order* in $(CH_3)_3CBr$. It is *zeroth order* in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus the overall reaction order is 1 + 0 = 1. What the reaction orders tell us in practical terms is that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has *no effect* on the reaction rate. (Again, when you work with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law *must* be determined experimentally.) Experimental data show that *k* has the value $5.15 \times 10^{-4}$ $s^{-1}$ at 25°C. The rate constant has units of reciprocal seconds ($s^{-1}$) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide ($CH_3Br$) is as follows:

$$rate = -\frac{\Delta\left[CH_3Br\right]}{\Delta t} = k'\left[CH_3Br\right]$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 14.2.11 is approximately $10^6$ times smaller than that for *t*-butyl bromide. Thus methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often change reaction conditions to obtain clues about what is occurring during a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing $OH^-$ ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. For methyl bromide, in contrast, the differential rate law becomes rate = $k''[CH_3Br][OH^-]$, with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, which again provides clues as to how the reactions differ on a molecular level.

### Note the Pattern

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements.

### Example 14.2.3

We present three reactions and their experimentally determined differential rate laws. For each reaction, give the *units* of the rate constant, give the reaction *order* with respect to each reactant, give the *overall reaction order*, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

1. $2HI\,(g) \overset{Pt}{\rightarrow} H_2\,(g) + I_2\,(g) rate = -\frac{1}{2}\frac{\Delta\left[HI\right]}{\Delta t} = k\left[HI\right]^2$
2. $2N_2O\,(g) \overset{\Delta}{\rightarrow} 2N_2\,(g) + O_2\,(g)$
   $rate = \frac{1}{2}\frac{\Delta\left[N_2O\right]}{\Delta t} = k$
3. $cyclopropane\,(g) \overset{\Delta}{\rightarrow} propane\,(g)$
   $rate = \frac{1}{2}\frac{\Delta\left[cyclopropance\right]}{\Delta t} = k\left[cyclopropane\right]$

**Given:** balanced chemical equations and differential rate laws

**Asked for:** units of rate constant, reaction orders, and effect of doubling reactant concentration

**Strategy:**

**A** Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

**B** Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Sum all exponents to obtain the overall reaction order.

**C** Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

**Solution:**

1. **A** $[HI]^2$ will give units of (moles per liter)$^2$. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]: $\frac{M}{s} = kM^2 \Rightarrow k = \frac{M/s}{M^2} = \frac{1}{M \cdot s} = M^{-1}s^{-1}$

   **B** The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

   **C** If the concentration of HI is doubled, the reaction rate will increase from $k[HI]_0^2$ to $k(2[HI])_0^2 = 4k[HI]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

   **B** The rate law tells us that the reaction rate is constant and independent of the $N_2O$ concentration. That is, the reaction is zeroth order in $N_2O$ and zeroth order overall.

   **C** Because the reaction rate is independent of the $N_2O$ concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds ($s^{-1}$) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1} = M/s$.

   **B** The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

   **C** Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

Exercise

Given the following two reactions and their experimentally determined differential rate laws: determine the *units* of the rate constant if time is in seconds, determine the reaction *order* with respect to each reactant, give the *overall reaction order*, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

1. $CH_3N = CH_3N\,(g) \rightarrow C_2H_6\,(g) + N_2\,(g)$
   $rate = -\frac{\Delta\,[CH_3N = CH_3N]}{\Delta t} = k\,[CH_3N = CH_3N]$
2. $2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$
   $rate = -\frac{\Delta\,[F_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta\,[NO_2]}{\Delta t} = k\,[NO_2]\,[F_2]$

**Answer**

1. $s^{-1}$; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.
2. $M^{-1}{\cdot}s^{-1}$; first order in $NO_2$, first order in $F_2$; second order overall; doubling $[NO_2]$ will double the reaction rate.

## Summary

Reaction rates are reported either as the **average rate** over a period of time or as the **instantaneous rate** at a single time.

The **rate law** for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a **differential rate law**, describing the change in reactant or product concentrations as a function of time, or as an **integrated rate law**, describing the actual concentrations of reactants or products as a function of time.

The **rate constant** ($k$) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The power to which a concentration is raised in a rate law indicates the **reaction order**, the degree to which the reaction rate depends on the concentration of a particular reactant.

## Key Takeaways

- Reaction rates can be determined over particular time intervals or at a given point in time.
- A rate law describes the relationship between reactant rates and reactant concentrations.

## Key Equations

**general definition of rate for A → B**

Equation 14.2.1: $rate = \frac{\Delta [B]}{\Delta t} = -\frac{\Delta [A]}{\Delta t}$

**general form of rate law when A and B are reactants**

Equation 14.2.6: $rate = k [A]^m [B]^n$

## Conceptual Problems

1. Explain why the reaction rate is generally fastest at early time intervals. For the second-order A + B → C, what would the plot of the concentration of C versus time look like during the course of the reaction?
2. Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?
3. Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of $10^{10}$ L/(mol·s). Would you expect the reactions to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $H_3O^+ + OH^- \rightarrow 2H_2O$ and $H_3O^+ + N(CH_3)_3 \rightarrow H_2O + HN(CH_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?
4. What information can you get from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?
5. During the hydrolysis reaction $A + H_2O \rightarrow B + C$, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How do you expect this effect to be reflected in the overall reaction order?

## Answers

1. Reactant concentrations are highest at the beginning of a reaction. The plot of [C] versus $t$ is a curve with a slope that becomes steadily less positive.
2. 
3. Faster in a less viscous solvent because the rate of diffusion is higher; the $H_3O^+/OH^-$ reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.
4. 
5. 

## Numerical Problems

1. The reaction rate of a particular reaction in which A and B react to make C is as follows:

   $rate = -\frac{\Delta [A]}{\Delta t} = \frac{1}{2}\frac{\Delta [C]}{\Delta t}$

   Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?
2. While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?

3. Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

| Time (s) | [A] (M) |
|---|---|
| 120 | 0.158 |
| 240 | 0.089 |
| 360 | 0.062 |

4. Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.
   1. $C_2H_5I \rightarrow C_2H_4 + HI$: rate = $k[C_2H_5I]$
   2. $SO + O_2 \rightarrow SO_2 + O$: rate = $k[SO][O_2]$
   3. $2CH_3 \rightarrow C_2H_6$: rate = $k[CH_3]^2$
   4. $ClOO \rightarrow Cl + O_2$: rate = $k$
5. Cleavage of $C_2H_6$ to produce two $CH_3\cdot$ radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with $k = 5.46 \times 10^{-4}\ s^{-1}$. How long will it take for the reaction to go to 15% completion? to 50% completion?
6. Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.

$$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+$$

$$O_2^+ + O \xrightarrow{k_2} O_2 + O^+$$

$$O^+ + N_2 \xrightarrow{k_3} N + NO^+$$

   Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[N_2^+][O_2]$, which one of the steps is rate limiting?
7. The oxidation of aqueous iodide by arsenic acid to give $I_3^-$ and arsenous acid proceeds via the following reaction:

$$H_3AsO_4\,(aq) + 3I^-\,(aq) + 2H^+\,(aq) \overset{k_f}{\rightleftharpoons} H_3AsO_3\,(aq) + I_3^-\,(aq) + H_2O\,(l)$$

   Write an expression for the initial rate of decrease of $[I_3^-]$, $\Delta[I_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [H_3AsO_3][I_3^-]/[H_3AsO_4][I^-]^3[H^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

## Answer

1.
2.
3.
4.
5. 298 s; 1270 s
6.
7.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 14.4: Methods of Determining Reaction Order

**Learning Objectives**

- To know how to determine the reaction order from experimental data.

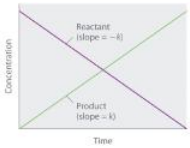
In the examples in this text, the exponents in the rate law are almost always the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data.

## Zeroth-Order Reactions

A zeroth-order reactionA reaction whose rate is independent of concentration. is one whose rate is independent of concentration; its differential rate law is rate = *k*. We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$rate = -\frac{\Delta [A]}{\Delta t} = -k\,[reactant]^0 = k(1) = k$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of −*k*. The value of *k* is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of *k*, a positive value.




**The graph of a zeroth-order reaction.** The change in concentration of reactant and product with time produces a straight line.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A_0] - kt$$

where $[A]_0$ is the initial concentration of reactant A. (Equation 14.3.2 has the form of the algebraic equation for a straight line, *y* = *mx* + *b*, with *y* = [A], *mx* = −*kt*, and *b* = $[A]_0$.) In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of $N_2O$ on a platinum (Pt) surface to produce $N_2$ and $O_2$, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O\,(g) \xrightarrow{Pt} 2N_2\,(g) + O_2\,(g)$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly $N_2O$ decomposes is the amount of Pt *surface* available (not the *amount* of Pt). As long as there is enough $N_2O$ to react with the entire Pt surface, doubling or quadrupling the $N_2O$ concentration will have no effect on the reaction rate.At very low concentrations of $N_2O$, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the $N_2O$ concentration. The reaction rate is as follows:

$$rate = -\frac{1}{2}\left(\frac{\Delta [N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta [N_2]}{\Delta t}\right) = \frac{\Delta [O_2]}{\Delta t} k\,[N_2O]^0 = k$$

Thus the rate at which $N_2O$ is consumed and the rates at which $N_2$ and $O_2$ are produced are independent of concentration. As shown in Figure 14.3.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the $N_2O$ concentration in the experimentally derived rate law is *not* the same as the reactant's stoichiometric

coefficient in the balanced chemical equation (2). For this reaction, as for all others, *the rate law must be determined experimentally*.

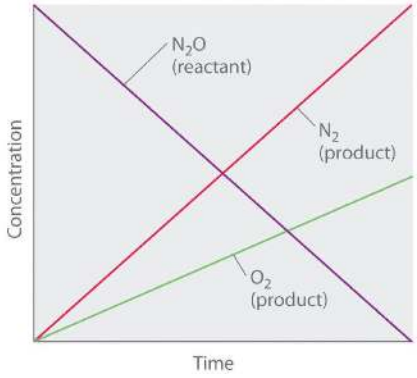



**Figure 14.3.2 A Zeroth-Order Reaction** This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of $N_2O$ to $N_2$ and $O_2$ on a Pt surface. The change in the concentrations of all species with time is linear.

## Note the Pattern

If a plot of reactant concentration versus time is linear, then the reaction is zeroth order in that reactant.

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the enzymeA catalyst that occurs naturally in living organisms and catalyzes biological reactions. alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

CH3COH(aq) + NH4+(aq)." href="/@api/deki/files/48697/6d8d2a62963267afdb3d7e7303345615.jpg">  CH3CN(l) + 2H2O(l) + H+(aq) - CH3COH(aq) + NH4+(aq)." style="width: 550px; height: 70px;" width="550px" height="70px" src="/@api/deki/files/48697/6d8d2a62963267afdb3d7e7303345615.jpg">

where $NAD^+$ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (part (a) in Figure 14.3.3). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 14.3.3).

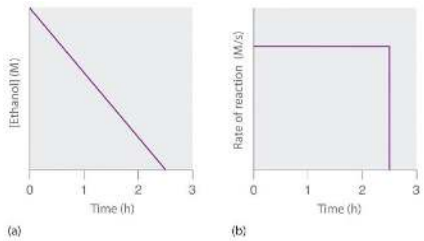



Figure 14.3.3 The Catalyzed Oxidation of Ethanol(a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. *In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.*
2. *A linear change in concentration with time is a clear indication of a zeroth-order reaction.*

## First-Order Reactions

In a first-order reactionA reaction whose rate is directly proportional to the concentration of one reactant., the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$rate = -\frac{\Delta [A]}{\Delta t} = k [A]^1 = k [A]$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds ($s^{-1}$).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$rate = [A] = [A_0]\, e^{-kt}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; $k$ is the rate constant; and $e$ is the base of the natural logarithms, which has the value 2.718 to three decimal places. (Essential Skills 6 in Section 11.9, discusses natural logarithms.) Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 14.20 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 14.20 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and $t$:

$$rate = ln [A] = ln [A_0] - kt$$

Because Equation 14.3.7 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of ln[A] versus $t$ for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 14.3.5) or the integrated rate law (Equation 14.3.7) can be used to determine whether a particular reaction is first order.

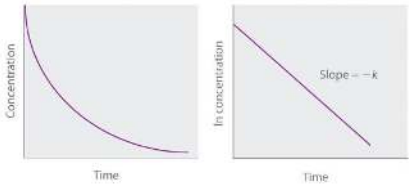
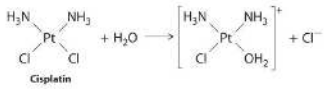



Figure 14.3.4 Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. In this chapter, we have already encountered two examples of first-order reactions: the hydrolysis of aspirin (Figure 14.2.1) and the reaction of *t*-butyl bromide with water to give *t*-butanol (Equation 14.7.7). Another reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:




Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 14.11 is important because cisplatin, the form in which the drug is administered, is *not* the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 14.11 have been studied extensively to find ways of maximizing the concentration of the active species.

### Note the Pattern

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 14.3.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin. Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 14.3.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ ($9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ ($9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = $k$[cisplatin]$^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 14.3.1. For example, substituting the values for Experiment 3 into Equation 14.19,

$$\mathbf{3.6 \times 10^{-5}\ M/min = \mathit{k}(0.024\ M)}$$

$$\mathbf{1.5 \times 10^{-3}\ min^{-1} = \mathit{k}}$$

**Table 14.3.1 Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C**

| Experiment | $[\text{Cisplatin}]_0$ (M) | Initial Rate (M/min) |
|---|---|---|
| 1 | 0.0060 | $9.0 \times 10^{-6}$ |
| 2 | 0.012 | $1.8 \times 10^{-5}$ |
| 3 | 0.024 | $3.6 \times 10^{-5}$ |
| 4 | 0.030 | $4.5 \times 10^{-5}$ |

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

### Example 14.3.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$CH_3CH_2Cl\,(g) \xrightarrow{\Delta} HCl\,(g) + C_2H_4\,(g)$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

| Experiment | $[CH_3CH_2Cl]_0$ (M) | Initial Rate (M/s) |
|---|---|---|
| 1 | 0.010 | $1.6 \times 10^{-8}$ |
| 2 | 0.015 | $2.4 \times 10^{-8}$ |
| 3 | 0.030 | $4.8 \times 10^{-8}$ |
| 4 | 0.040 | $6.4 \times 10^{-8}$ |

**Given:** balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

**Asked for:** reaction order and rate constant

**Strategy:**

**A** Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

**B** Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

**C** Use measured concentrations and rate data from any of the experiments to find the rate constant.

**Solution:**

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

**A** Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

**B** This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

**C** We can calculate the rate constant ($k$) using any row in the table. Selecting Experiment 1 gives the following:

$$\mathbf{1.60 \times 10^{-8}\ M/s = \mathit{k}(0.010\ M)\ 1.6 \times 10^{-6}\ s^{-1} = \mathit{k}}$$

Exercise

Sulfuryl chloride ($SO_2Cl_2$) decomposes to $SO_2$ and $Cl_2$ by the following reaction:

$$\mathbf{SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)}$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

| Experiment | $[SO_2Cl_2]_0$ (M) | Initial Rate (M/s) |
|---|---|---|
| 1 | 0.0050 | $1.10 \times 10^{-7}$ |
| 2 | 0.0075 | $1.65 \times 10^{-7}$ |
| 3 | 0.0100 | $2.20 \times 10^{-7}$ |
| 4 | 0.0125 | $2.75 \times 10^{-7}$ |

**Answer:** first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

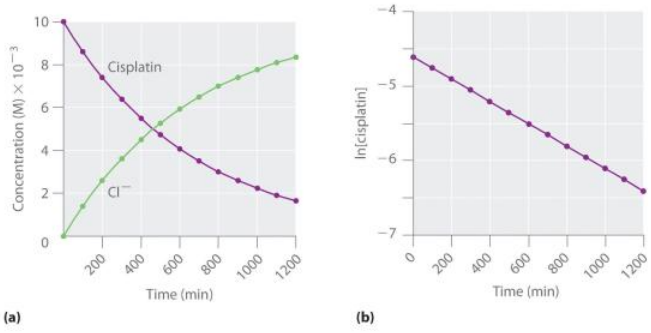



Figure 14.3.5 The Hydrolysis of Cisplatin, a First-Order **Reaction** These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Part (a) in Figure 14.3.5 shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C. The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 14.3.5. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to

calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 14.3.5 for $t$ = 100 min ([cisplatin] = 0.0086 M) and $t$ = 1000 min ([cisplatin] = 0.0022 M),

$$slope = \frac{ln\,[cisplatin]_{1000} - ln\,[cisplatin]_{100}}{1000\ min - 100\ min}$$

$$-k = \frac{ln0.0022 - ln0.0086}{1000\ min - 100\ min} = \frac{-6.12 - (-4.76)}{900\ min} = -1.51 \times 10^{-3} min^{-1}$$

$$k = 1.51 \times 10^{-3}\ min^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of $min^{-1}$ because the times plotted on the horizontal axes in parts (a) and (b) in Figure 14.3.5 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

### Example 14.3.2

Refer back to Example 4. If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M? (Recall that we calculated the rate constant for this reaction in Example 4.)

**Given:** initial concentration, rate constant, and time interval

**Asked for:** concentration at specified time and time required to obtain particular concentration

**Strategy:**

**A** Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction ($k$) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time $t$.

**B** Given a concentration [A], solve the integrated rate law for time $t$.

**Solution:**

The exponential form of the integrated rate law for a first-order reaction (Equation 14.3.6) is $[A] = [A]_0 e^{-kt}$.

**A** Having been given the initial concentration of ethyl chloride ($[A]_0$) and having calculated the rate constant in Example 4 ($k$ = 1.6 × $10^{-6}$ $s^{-1}$), we can use the rate law to calculate the concentration of the reactant at a given time $t$. Substituting the known values into the integrated rate law,

$$[CH_3CH_2Cl]_{10\ h} = [CH_3CH_2Cl]_0\, e^{-kt}$$

$$= 0.0200\ M\ exp\left[\left(-1.6 \times 10^{-6}\ s^{-1}\right)(10\ h)\,(60\ min/h)\,(60\ s/min)\right]$$

\( = 0.0189\;M

We could also have used the logarithmic form of the integrated rate law (Equation 14.3.7):

$$ln\,[CH_3CH_2Cl]_{10\ h} = ln\,[CH_3CH_2Cl]_0 - kt$$

$$= ln0.0200\ M - \left(-1.6 \times 10^{-6}\ s^{-1}\right)(10\ h)\,(60\ min/h)\,(60\ s/min)$$

$$= -3.912 - -0.0576 = -3.970$$

$$[CH_3CH_2Cl]_{10\ h} = e^{-3.970}\ M$$

=0.0189\;M

**B** To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for $t$. Equation 14.3.7 gives the following:

$$ln\,[CH_3CH_2Cl]_t = ln\,[CH_3CH_2Cl]_0 - kt$$

$$kt = ln\,[CH_3CH_2Cl]_0 - ln\,[CH_3CH_2Cl]_t = ln\,\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\,ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t} = \frac{1}{1.6 \times 10^{-6}\ s^{-1}}\,ln\frac{0.0200\ M}{0.0050\ M}$$

$$t = \frac{ln\ 4.0}{k} = 8.7 \times 10^5\ s = 240\ h = 2.4 \times 10^2\ h$$

Exercise

In the exercise in Example 4, you found that the decomposition of sulfuryl chloride ($SO_2Cl_2$) is first order, and you calculated the rate constant at 320°C. Use the form(s) of the integrated rate law to find the amount of $SO_2Cl_2$ that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C. How long would it take for 90% of the $SO_2Cl_2$ to decompose?

**Answer:** 0.0252 M; 29 h

## Second-Order Reactions

The simplest kind of second-order reactionA reaction whose rate is proportional to the square of the concentration of the reactant (for a reaction with the general form 2A → products) or is proportional to the product of the concentrations of two reactants (for a reaction with the general form A + B → products). is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form 2A → products. A second kind of second-order reaction has a reaction rate that is proportional to the *product* of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a *dimerization reaction*, in which two smaller molecules, each called a *monomer*, combine to form a larger molecule (a *dimer*).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$rate = -\frac{\Delta\,[A]}{2\Delta t} = k\,[reactant]^2$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A_0]} + kt$$

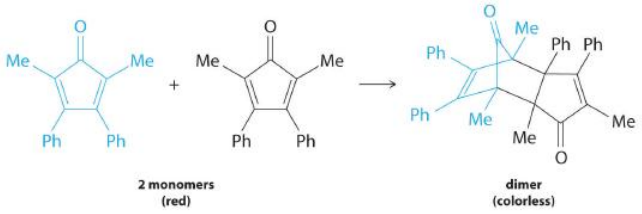
Because Equation 14.3.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus $t$ for a simple second-order reaction is a straight line with a slope of $k$ and an intercept of $1/[A]_0$.

### Note the Pattern

Second-order reactions generally have the form 2A → products or A + B → products.

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of $NO_2$ to NO and $O_2$ and the decomposition of HI to $I_2$ and $H_2$. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:




For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively.The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of

drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 14.3.8) or the integrated rate law (Equation 14.3.9).

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 14.3.2 . From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ M/min}{1.8 \times 10^{-5}\ M/mi} = 2.8 \ \ and \ \ \frac{3.4 \times 10^{-3}\ M/min}{2.0 \times 10^{-3}\ M/mi} = 1.7$$

**Table 14.3.2 Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M**

| Time (min) | [Monomer] (M) | Instantaneous Rate (M/min) |
|---|---|---|
| 10 | 0.0044 | $8.0 \times 10^{-5}$ |
| 26 | 0.0034 | $5.0 \times 10^{-5}$ |
| 44 | 0.0027 | $3.1 \times 10^{-5}$ |
| 70 | 0.0020 | $1.8 \times 10^{-5}$ |
| 120 | 0.0014 | $8.0 \times 10^{-6}$ |

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$rate \ \alpha \ \ [monomer]^2$$

This means that the reaction is second order in the monomer. Using Equation 14.3.8 and the data from any row in Table 14.3.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$rate = k\,[A^2]$$

$$8.0 \times 10^{-5}\ M/min = k\left(4.4 \times 10^{-3}\ M\right)$$

$$4.1\ min^{-1} = k$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in part (a) in Figure 14.3.6. The measurements show that the concentration of the monomer (initially $5.4 \times 10^{-3}$ M) decreases with increasing time. This graph also shows that the reaction *rate* decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in part (b) in Figure 14.3.6. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k$ = 4.1 $M^{-1}{\cdot}min^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. *The reaction order must always be determined experimentally.*

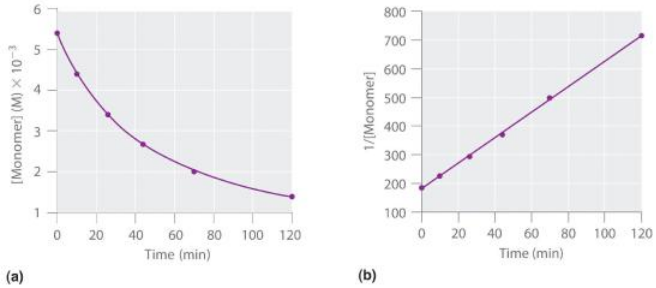



Figure 14.13 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the *same order*, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders. The differential and integrated rate laws for zeroth-, first-, and second-order reactions and their corresponding graphs are shown in Figure 14.4.2 in Section 14.4.

### Example 14.3.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2NO_2\,(g) \xrightarrow{\Delta} 2NO\,(g) + O_2\,(g)$$

Experimental data for the reaction at 300°C and four initial concentrations of $NO_2$ are listed in the following table:

| Experiment | $[NO_2]_0$ (M) | Initial Rate (M/s) |
|---|---|---|
| 1 | 0.015 | $1.22 \times 10^{-4}$ |
| 2 | 0.010 | $5.40 \times 10^{-5}$ |
| 3 | 0.0080 | $3.46 \times 10^{-5}$ |
| 4 | 0.0050 | $1.35 \times 10^{-5}$ |

Determine the reaction order and the rate constant.

**Given:** balanced chemical equation, initial concentrations, and initial rates

**Asked for:** reaction order and rate constant

**Strategy:**

**A** From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

**B** Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant ($k$).

**Solution:**

**A** We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in $NO_2$ concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

**B** We have rate = $k[NO_2]^2$. We can calculate the rate constant ($k$) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$rate = k\,[NO_2]^2$$

$$5.40 \times 10^{-5}\ M/s = k\,(0.010\ M)^2$$

$$0.540\ M^{-1}s^{-1} = k$$

Exercise

When the highly reactive species $HO_2$ forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$2HO_2(g) \rightarrow H_2O_2(g) + O_2(g)$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

| Experiment | $[HO_2]_0$ (M) | Initial Rate (M/s) |
|---|---|---|
| 1 | $1.1 \times 10^{-8}$ | $1.7 \times 10^{-7}$ |
| 2 | $2.5 \times 10^{-8}$ | $8.8 \times 10^{-7}$ |
| 3 | $3.4 \times 10^{-8}$ | $1.6 \times 10^{-6}$ |
| 4 | $5.0 \times 10^{-8}$ | $3.5 \times 10^{-6}$ |

Determine the reaction order and the rate constant.

**Answer:** second order in $HO_2$; $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$

### Note the Pattern

If a plot of reactant concentration versus time is not linear but a plot of 1/reaction concentration versus time is linear, then the reaction is second order.

### Example 14.3.4

If a flask that initially contains 0.056 M $NO_2$ is heated at 300°C, what will be the concentration of $NO_2$ after 1.0 h? How long will it take for the concentration of $NO_2$ to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 14.3.9) and the rate constant calculated in Example 6.

**Given:** balanced chemical equation, rate constant, time interval, and initial concentration

**Asked for:** final concentration and time required to reach specified concentration

**Strategy:**

**A** Given $k$, $t$, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].

**B** Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for $t$.

**Solution:**

**A** We know $k$ and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at $t$ = 1 h (3600 s). Substituting the appropriate values into Equation 14.3.9,

$$\frac{1}{[NO_2]_{3600}} = \frac{1}{[NO_2]_0} + kt = \frac{1}{0.056\ M} + (0.54\ M^{-1}s^{-1})\,(3600\ s)$$

$$= 2.0 \times 10^{-3}\ M^{-1}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

**B** In this case, we know $k$ and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056$ M. To do this, we solve Equation 14.3.9 for $t$, using the concentrations given.

$$\frac{\frac{1}{[NO_2]_{3600}} - \frac{1}{[NO_2]_0}}{k} = \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1}s^{-1}} = 3.0 \times 10^2\ s = 5\ min$$

$NO_2$ decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise

In the exercise in Example 6, you calculated the rate constant for the decomposition of $HO_2$ as $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$. This high rate constant means that $HO_2$ decomposes rapidly under the reaction conditions given in the problem. In fact, the $HO_2$ molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of $HO_2$, calculate the concentration of $HO_2$ that remains after 1.0 h at 25°C. How long will it take for 90% of the $HO_2$ to decompose? Use the integrated rate law for a second-order reaction (Equation 14.3.9) and the rate constant calculated in the exercise in Example 6.

**Answer:** $2.0 \times 10^{-13}$ M; $6.4 \times 10^{-6}$ s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form A + B → products, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$rate = -\frac{\Delta [A]}{\Delta t} = -\frac{\Delta [B]}{\Delta t} = k [A] [B]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant. We presented one example at the end of Section 14.2, the reaction of $CH_3Br$ with $OH^-$ to produce $CH_3OH$.

## Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding reaction mechanismsThe sequence of events that occur at the molecular level during a reaction. can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction A + B → products, for example, we need to determine *k* and the exponents *m* and *n* in the following equation:

$$rate = k [A]^m [B]^n$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments.

Rate data for a hypothetical reaction of the type A + B → products are given in Table 14.3.3. The general rate law for the reaction is given in Equation 14.3.11. We can obtain *m* or *n* directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 14.3.3.

**Table 14.3.3 Rate Data for a Hypothetical Reaction of the Form A + B → Products**

| Experiment | [A] (M) | [B] (M) | Initial Rate (M/min) |
|---|---|---|---|
| 1 | 0.50 | 0.50 | $8.5 \times 10^{-3}$ |
| 2 | 0.75 | 0.50 | $19 \times 10^{-3}$ |
| 3 | 1.00 | 0.50 | $34 \times 10^{-3}$ |
| 4 | 0.50 | 0.75 | $8.5 \times 10^{-3}$ |
| 5 | 0.50 | 1.00 | $8.5 \times 10^{-3}$ |

$$\frac{rate^1}{rate^3} = \frac{k [A^1]^m [B^1]^n}{k [A^3]^m [B^3]^n}$$

Inserting the appropriate values from Table 14.3.3,

$$\frac{8.5 \times 10^{-3} \ \cancel{M/min}}{34. \times 10^{-3} \ \cancel{M/min}} = \frac{k \left[0.50 \ \cancel{M}\right]^m \ \cancel{[0.50 \ M]^n}}{k \left[1.00 \ \cancel{M}\right]^m \ \cancel{[0.50 \ M]^n}}$$

Because 1.00 to any power is 1, $[1.00 \text{ M}]^m = 1.00$ M. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for *m*.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for *n*.

$$\frac{rate^1}{rate^3} = \frac{k\left[A^1\right]^m\left[B^1\right]^n}{k\left[A^5\right]^m\left[B^5\right]^n}$$

Substituting the appropriate values from Table 14.3.3,

$$\frac{8.5 \times 10^{-3}\ \cancel{M/min}}{8.5 \times 10^{-3}\ \cancel{M/min}} = \frac{k\left[0.50\ \cancel{M}\right]^m\left[05.0\ \cancel{M}\right]^n}{k\left[0.50\ \cancel{M}\right]^m\left[1.00\ \cancel{M}\right]^n}$$

Canceling leaves 1.0 = $[0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$rate = k\left[A\right]^2\left[B\right]^0$$

We can now calculate the rate constant by inserting the data from any row of Table 14.3.3into the experimentally determined rate law and solving for *k*. Using Experiment 2, we obtain

$$19. \times 10^{-}3\ M/min = k\,(0.75\ M)^2$$

$$3.4 \times 10^{-}2\ M^{-1}min^{-1} = k$$

You should verify that using data from any other row of Table 14.3.3 gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

### Example 14.3.5

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with $O_2$ to give $NO_2$, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2NO + O_2 \longrightarrow 2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with $O_2$ at 25°C:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Determine the rate law for the reaction and calculate the rate constant.

| Experiment | $[NO]_0$ (M) | $[O_2]_0$ (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1 | 0.0235 | 0.0125 | $7.98 \times 10^{-3}$ |
| 2 | 0.0235 | 0.0250 | $15.9 \times 10^{-3}$ |
| 3 | 0.0470 | 0.0125 | $32.0 \times 10^{-3}$ |
| 4 | 0.0470 | 0.0250 | $63.5 \times 10^{-3}$ |

**Given:** balanced chemical equation, initial concentrations, and initial rates

**Asked for:** rate law and rate constant

**Strategy:**

**A** Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.

**B** Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

**Solution:**

**A** Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in $O_2$. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$rate = k\,[NO]^2\,[O_2]$$

**B** The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{k}{[NO]^2\,[O_2]} = \frac{7.98 \times 10{-}3\ M/s}{(0.0235\ M)^2\,(0.0125\ M)} = 1.16 \times 103\ M^{-2}s^{-1}$$

The overall reaction order ($m + n$) is 3, so this is a third-order reaction, a reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Exercise

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O_8^{2-}\,(aq) + 3I^-\,(aq) \rightarrow 2SO_4^{2-}\,(aq) + I_3^-\,(aq)$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

| Experiment | $[S_2O_8^{2-}]_0$ (M) | $[I^-]_0$ (M) | Initial Rate (M/s) |
|---|---|---|---|
| 1 | 0.27 | 0.38 | 2.05 |
| 2 | 0.40 | 0.38 | 3.06 |
| 3 | 0.40 | 0.22 | 1.76 |

**Answer:** rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ M^{-1}{\cdot}s^{-1}$

## Summary

The reaction rate of a **zeroth-order reaction** is independent of the concentration of the reactants. The reaction rate of a **first-order reaction** is directly proportional to the concentration of one reactant. The reaction rate of a simple **second-order reaction** is proportional to the square of the concentration of one reactant. Knowing the **rate law** of a reaction gives clues to the **reaction mechanism**.

## Key Takeaway

- Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data.

## Key Equations

**zeroth-order reaction**

Equation 14.3.1 $rate = -\frac{\Delta\,[A]}{\Delta t} = k$

Equation 14.3.2: $[A] = [A_0] - kt$

**first-order reaction**

Equation 14.3.5: $rate = -\frac{\Delta\,[A]}{\Delta t} = k\,[A]$

Equation 14.3.6: $[A] = [A_0]\,e^{-kt}$

Equation 14.3.7: $ln\,[A] = ln\,[A_0] - kt$

**second-order reaction**

Equation 14.3.8: $ln\,[A] = ln\,[A_0] + kt$

Equation 14.3.9: $\frac{1}{[A]} = \frac{1}{[A_0]} + kt$

## Conceptual Problems

1. What are the characteristics of a zeroth-order reaction? Experimentally, how would you determine whether a reaction is zeroth order?
2. Predict whether the following reactions are zeroth order and explain your reasoning.
    1. a substitution reaction of an alcohol with HCl to form an alkyl halide and water
    2. catalytic hydrogenation of an alkene
    3. hydrolysis of an alkyl halide to an alcohol
    4. enzymatic conversion of nitrate to nitrite in a soil bacterium
3. In a first-order reaction, what is the advantage of using the integrated rate law expressed in natural logarithms over the rate law expressed in exponential form?
4. If the reaction rate is directly proportional to the concentration of a reactant, what does this tell you about (a) the reaction order with respect to the reactant and (b) the overall reaction order?
5. The reaction of NO with $O_2$ is found to be second order with respect to NO and first order with respect to $O_2$. What is the overall reaction order? What is the effect of doubling the concentration of each reagent on the reaction rate?

## Numerical Problems

1. Iodide reduces Fe(III) according to the following reaction:

    $2Fe^{3+}(soln) + 2I^{-}(soln) \rightarrow 2Fe^{2+}(soln) + I_2(soln)$

    Experimentally, it was found that doubling the concentration of Fe(III) doubled the reaction rate, and doubling the iodide concentration increased the reaction rate by a factor of 4. What is the reaction order with respect to each species? What is the overall rate law? What is the overall reaction order?

2. Benzoyl peroxide is a medication used to treat acne. Its rate of thermal decomposition at several concentrations was determined experimentally, and the data were tabulated as follows:

| Experiment | $[\text{Benzoyl Peroxide}]_0$ (M) | Initial Rate (M/s) |
|---|---|---|
| 1 | 1.00 | $2.22 \times 10^{-4}$ |
| 2 | 0.70 | $1.64 \times 10^{-4}$ |
| 3 | 0.50 | $1.12 \times 10^{-4}$ |
| 4 | 0.25 | $0.59 \times 10^{-4}$ |

    What is the reaction order with respect to benzoyl peroxide? What is the rate law for this reaction?

3. 1-Bromopropane is a colorless liquid that reacts with $S_2O_3^{2-}$ according to the following reaction:

    $C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^{-} + Br^{-}$

    The reaction is first order in 1-bromopropane and first order in $S_2O_3^{2-}$, with a rate constant of $8.05 \times 10^{-4}\ M^{-1}{\cdot}s^{-1}$. If you began a reaction with 40 mmol/100 mL of $C_3H_7Br$ and an equivalent concentration of $S_2O_3^{2-}$, what would the initial reaction rate be? If you were to decrease the concentration of each reactant to 20 mmol/100 mL, what would the initial reaction rate be?

4. The experimental rate law for the reaction $3A + 2B \rightarrow C + D$ was found to be $\Delta[C]/\Delta t = k[A]^2[B]$ for an overall reaction that is third order. Because graphical analysis is difficult beyond second-order reactions, explain the procedure for determining the rate law experimentally.

## Answers

1. First order in $Fe^{3+}$; second order in $I^-$; third order overall; rate = $k[Fe^{3+}][I^-]^2$.
2. 
3. $1.29 \times 10^{-4}$ M/s; $3.22 \times 10^{-5}$ M/s
4. 

## Contributors

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# 14.5: Using Graphs to Determine Rate Laws, Rate Constants and Reaction Orders

**Learning Objectives**

- To use graphs to analyze the kinetics of a reaction.

In Section 14.3, you learned that the integrated rate law for each common type of reaction (zeroth, first, or second order in a single reactant) can be plotted as a straight line. Using these plots offers an alternative to the methods described for showing how reactant concentration changes with time and determining reaction order.

We will illustrate the use of these graphs by considering the thermal decomposition of $NO_2$ gas at elevated temperatures, which occurs according to the following reaction:

$$2NO_2\,(g) \xrightarrow{\Delta} 2NO\,(g) + O_2\,(g)$$

Experimental data for this reaction at 330°C are listed in Table 14.4.1; they are provided as $[NO_2]$, $\ln[NO_2]$, and $1/[NO_2]$ versus time to correspond to the integrated rate laws for zeroth-, first-, and second-order reactions, respectively. The actual concentrations of $NO_2$ are plotted versus time in part (a) in Figure 14.4.1. Because the plot of $[NO_2]$ versus $t$ is not a straight line, we know the reaction is not zeroth order in $NO_2$. A plot of $\ln[NO_2]$ versus $t$ (part (b) in Figure 14.4.1) shows us that the reaction is not first order in $NO_2$ because a first-order reaction would give a straight line. Having eliminated zeroth-order and first-order behavior, we construct a plot of $1/[NO_2]$ versus $t$ (part (c) in Figure 14.4.1). This plot is a straight line, indicating that the reaction is second order in $NO_2$.

**Table 14.4.1 Concentration of $NO_2$ as a Function of Time at 330°C**

| Time (s) | $[NO_2]$ (M) | $\ln[NO_2]$ | $1/[NO_2]$ ($M^{-1}$) |
|---|---|---|---|
| 0 | $1.00 \times 10^{-2}$ | −4.605 | 100 |
| 60 | $6.83 \times 10^{-3}$ | −4.986 | 146 |
| 120 | $5.18 \times 10^{-3}$ | −5.263 | 193 |
| 180 | $4.18 \times 10^{-3}$ | −5.477 | 239 |
| 240 | $3.50 \times 10^{-3}$ | −5.655 | 286 |
| 300 | $3.01 \times 10^{-3}$ | −5.806 | 332 |
| 360 | $2.64 \times 10^{-3}$ | −5.937 | 379 |

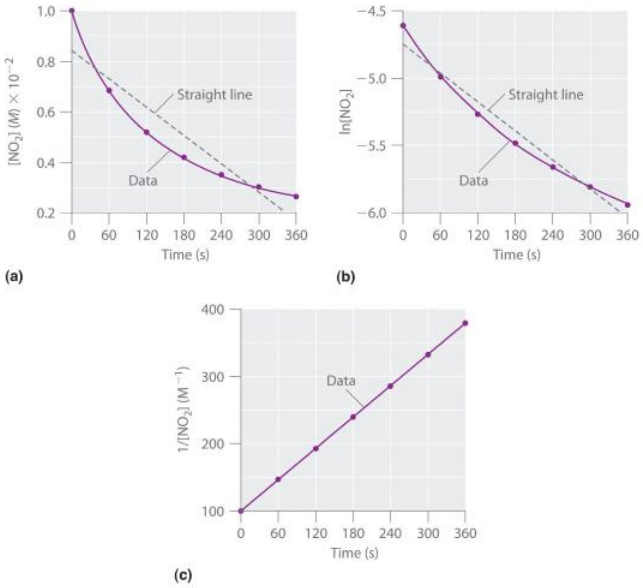



Figure 14.4.1 The Decomposition of $NO_2$ These plots show the decomposition of a sample of $NO_2$ at 330°C as (a) the concentration of $NO_2$ versus *t*, (b) the natural logarithm of $[NO_2]$ versus *t*, and (c) $1/[NO_2]$ versus *t*.

We have just determined the reaction order using data from a single experiment by plotting the concentration of the reactant as a function of time. Because of the characteristic shapes of the lines shown in Figure 14.4.2, the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method described in Section 14.3 required multiple experiments at different $NO_2$ concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.

| | Zeroth Order | First Order | Second Order |
|---|---|---|---|
| **Differential rate law** | $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$ | $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$ | $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$ |
| **Concentration vs. time** |  |  |  |
| **Integrated rate law** | $[A] = [A]_0 - kt$ | $[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$ | $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ |
| **Straight-line plot to determine rate constant** |  |  |  |
| **Relative rate vs. concentration** | [A], *M* / Rate, M/s<br>1 / 1<br>2 / 1<br>3 / 1 | [A], *M* / Rate, M/s<br>1 / 1<br>2 / 2<br>3 / 3 | [A], *M* / Rate, M/s<br>1 / 1<br>2 / 4<br>3 / 9 |
| **Half-life** | $t_{1/2} = \frac{[A]_0}{2k}$ | $t_{1/2} = \frac{0.693}{k}$ | $t_{1/2} = \frac{1}{k[A]_0}$ |
| **Units of *k*, rate constant** | M/s | 1/s | $M^{-1}s^{-1}$ |

Figure 14.4.2 Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws

## Example 14.4.1

Dinitrogen pentoxide ($N_2O_5$) decomposes to $NO_2$ and $O_2$ at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln) \rightarrow 4NO_2\,(soln) + O_2\,(g)$$

This reaction is carried out in a $CCl_4$ solution at 45°C. The concentrations of $N_2O_5$ as a function of time are listed in the following table, together with the natural logarithms and reciprocal $N_2O_5$ concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

| Time (s) | $[N_2O_5]$ (M) | $\ln[N_2O_5]$ | $1/[N_2O_5]$ ($M^{-1}$) |
|---|---|---|---|
| 0 | 0.0365 | −3.310 | 27.4 |
| 600 | 0.0274 | −3.597 | 36.5 |
| 1200 | 0.0206 | −3.882 | 48.5 |
| 1800 | 0.0157 | −4.154 | 63.7 |
| 2400 | 0.0117 | −4.448 | 85.5 |
| 3000 | 0.00860 | −4.756 | 116 |
| 3600 | 0.00640 | −5.051 | 156 |

**Given:** balanced chemical equation, reaction times, and concentrations

**Asked for:** graph of data, rate law, and rate constant

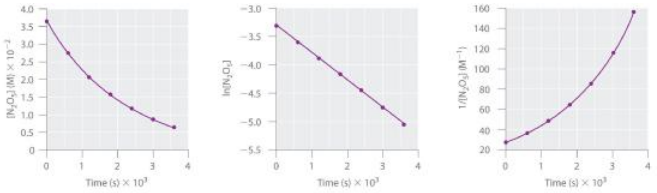
**Strategy:**

**A** Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 14.4.2 to determine the reaction order.

**B** Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

**Solution:**

**A** Here are plots of $[N_2O_5]$ versus $t$, $\ln[N_2O_5]$ versus $t$, and $1/[N_2O_5]$ versus $t$:



The plot of $\ln[N_2O_5]$ versus $t$ gives a straight line, whereas the plots of $[N_2O_5]$ versus $t$ and $1/[N_2O_5]$ versus $t$ do not. This means that the decomposition of $N_2O_5$ is first order in $[N_2O_5]$.

**B** The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus $t$ for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus $t$. Using the points for $t$ = 0 and 3000 s,

$$slope = \frac{ln\,[N_2O_5]_{3000} - ln\,[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ s^{-1}$$

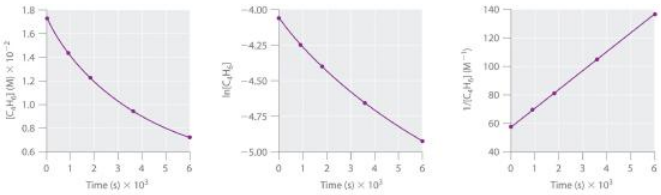
Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

Exercise

1,3-Butadiene ($CH_2$=CH—CH=$CH_2$; $C_4H_6$) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of $C_4H_6$ as a function of time at 326°C are listed in the following table along with $\ln[C_4H_6]$ and the reciprocal concentrations. Graph the data as concentration versus $t$, ln concentration versus $t$, and 1/concentration versus $t$. Then determine the reaction order in $C_4H_6$, the rate law, and the rate constant for the reaction.

| Time (s) | $[C_4H_6]$ (M) | $\ln[C_4H_6]$ | $1/[C_4H_6]$ ($M^{-1}$) |
|---|---|---|---|
| 0 | $1.72 \times 10^{-2}$ | −4.063 | 58.1 |
| 900 | $1.43 \times 10^{-2}$ | −4.247 | 69.9 |
| 1800 | $1.23 \times 10^{-2}$ | −4.398 | 81.3 |
| 3600 | $9.52 \times 10^{-3}$ | −4.654 | 105 |
| 6000 | $7.30 \times 10^{-3}$ | −4.920 | 137 |

**Answer**



second order in $C_4H_6$; rate = $k[C_4H_6]^2$; $k = 1.3 \times 10^{-2}\ M^{-1}{\cdot}s^{-1}$

## Summary

For a zeroth-order reaction, a plot of the concentration of any reactant versus time is a straight line with a slope of $-k$. For a first-order reaction, a plot of the natural logarithm of the concentration of a reactant versus time is a straight line with a slope of $-k$. For a second-order reaction, a plot of the inverse of the concentration of a reactant versus time is a straight line with a slope of $k$.

## Key Takeaway

- Plotting the concentration of a reactant as a function of time produces a graph with a characteristic shape that can be used to identify the reaction order in that reactant.

## Conceptual Problems

1. Compare first-order differential and integrated rate laws with respect to the following. Is there any information that can be obtained from the integrated rate law that cannot be obtained from the differential rate law?
    1. the magnitude of the rate constant
    2. the information needed to determine the order
    3. the shape of the graphs
2. In the single-step, second-order reaction 2A → products, how would a graph of [A] versus time compare to a plot of 1/[A] versus time? Which of these would be the most similar to the same set of graphs for A during the single-step, second-order reaction A + B → products? Explain.
3. For reactions of the same order, what is the relationship between the magnitude of the rate constant and the reaction rate? If you were comparing reactions with different orders, could the same arguments be made? Why?

## Answers

1. 1. For a given reaction under particular conditions, the magnitude of the first-order rate constant does not depend on whether a differential rate law or an integrated rate law is used.
    2. The differential rate law requires multiple experiments to determine reactant order; the integrated rate law needs only one experiment.
    3. Using the differential rate law, a graph of concentration versus time is a curve with a slope that becomes less negative with time, whereas for the integrated rate law, a graph of ln[reactant] versus time gives a straight line with slope = $-k$. The integrated rate law allows you to calculate the concentration of a reactant at any time during the reaction; the differential rate law does not.

2.

3. The reaction rate increases as the rate constant increases. We cannot directly compare reaction rates and rate constants for reactions of different orders because they are not mathematically equivalent.

## Numerical Problems

1. One method of using graphs to determine reaction order is to use relative rate information. Plotting the log of the relative rate versus log of relative concentration provides information about the reaction. Here is an example of data from a zeroth-order reaction:

| Relative [A] (M) | Relative Rate (M/s) |
|---|---|
| 1 | 1 |
| 2 | 1 |
| 3 | 1 |

   Varying [A] does not alter the reaction rate. Using the relative rates in the table, generate plots of log(rate) versus log(concentration) for zeroth-, first- and second-order reactions. What does the slope of each line represent?

2. The table below follows the decomposition of $N_2O_5$ gas by examining the partial pressure of the gas as a function of time at 45°C. What is the reaction order? What is the rate constant? How long would it take for the pressure to reach 105 mmHg at 45°C?

| Time (s) | Pressure (mmHg) |
|---|---|
| 0 | 348 |
| 400 | 276 |
| 1600 | 156 |
| 3200 | 69 |
| 4800 | 33 |

## Contributors

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Modified by Joshua B. Halpern

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# 14.6: Half Lives and Radioactive Decay Kinetics

**Learning Objectives**

- To know how to use half-lives to describe the rates of first-order reactions.

## Half-Lives

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the half-lifeThe period of time it takes for the concentration of a reactant to decrease to one-half its initial value. of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_0/2$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is *independent of the concentration of the reactants*. This becomes evident when we rearrange the integrated rate law for a first-order reaction (Equation 14.3.6) to produce the following equation:

$$ln\frac{[A]_0}{[A]} = kt$$

Substituting $[A]_0/2$ for [A] and $t_{1/2}$ for $t$ (to indicate a half-life) into Equation 14.5.1 gives

$$ln\frac{[A]_0}{[A]_0/2} = ln2 = kt_{1/2}$$

The natural logarithm of 2 (to three decimal places) is 0.693. Substituting this value into the equation, we obtain the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure 14.5.1 "The Half-Life of a First-Order Reaction", and is independent of [A].

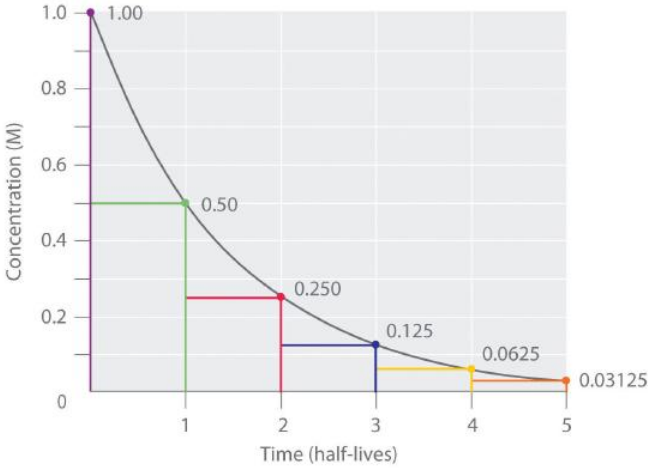



Figure 14.5.1 The Half-Life of a First-Order **Reaction** This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

| Number of Half-Lives | Percentage of Reactant Remaining | |
|---|---|---|
| 1 | $\frac{100\%}{2} = 50\%$ | $\frac{1}{2}(100\%) = 50\%$ |
| 2 | $\frac{50\%}{2} = 25\%$ | $\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$ |
| 3 | $\frac{25\%}{2} = 12.5\%$ | $\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$ |
| *n* | $\frac{100\%}{2^n}$ | $\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$ |

As you can see from this table, the amount of reactant left after *n* half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

### Note the Pattern

For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].

### Example 14.5.1

The anticancer drug cisplatin hydrolyzes in water with a rate constant of $1.5 \times 10^{-3}$ $min^{-1}$ at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cisplatin has a concentration of 0.053 M, what will be the concentration of cisplatin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

**Given:** rate constant, initial concentration, and number of half-lives

**Asked for:** half-life, final concentrations, and percent completion

**Strategy:**

**A** Use Equation 14.5.3 to calculate the half-life of the reaction.

**B** Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.

**C** Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

**Solution:**

**A** We can calculate the half-life of the reaction using Equation 14.5.3:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ min^{-1}} = 4.6 \times 10^2\ min$$

Thus it takes almost 8 h for half of the cisplatin to hydrolyze.

**B** After 5 half-lives (about 38 h), the remaining concentration of cisplatin will be as follows:

$$\frac{0.053\ M}{2^5} = \frac{0.053\ M}{32} = 0.0017\ M$$

After 10 half-lives (77 h), the remaining concentration of cisplatin will be as follows:

$$\frac{0.053\ M}{2^{10}} = \frac{0.053\ M}{1024} = 5.2 \times 10^{-5}\ M$$

**C** The percent completion after 5 half-lives will be as follows:

$$percent\ completion = \frac{(0.053\ M - 0.0017\ M)\,100}{0.53\ M} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$percent\ completion = \frac{(0.053\ M - 5.2 \times 10^{-5}\ M)\,100}{0.53\ M} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

Exercise

In Example 4 you found that ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of 1.6 × $10^{-6}$ $s^{-1}$ at 650°C. What is the half-life for the reaction under these conditions? If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

**Answer:** 4.3 × $10^5$ s = 120 h = 5.0 days; 4.8 × $10^{-3}$ M

## Radioactive Decay Rates

As you learned in Chapter 1 radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using *N* to represent the number of atoms of the radioactive isotope, we can define the rate of decayThe decrease in the number of a radioisotope's nuclei per unit time. of the sample, which is also called its activity (*A*)The decrease in the number of a radioisotope's nuclei per unit time: A=−ΔN/Δt as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t}$$

Activity is usually measured in *disintegrations per second (dps) or disintegrations per minute (dpm)*.

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN$$

Here, the symbol *k* is the *radioactive decay constant*, which has units of inverse time (e.g., $s^{-1}$, $yr^{-1}$) and a characteristic value for each radioactive isotope. If we combine Equation 14.5.4 and Equation 14.5.6 we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN$$

Equation 14.5.6 is the same as the equation for the reaction rate of a first-order reaction (Equation 14.3.5), except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay *is* a first-order process and can be described in terms of either the differential rate law (Equation 14.4.7) or the integrated rate law:

$$N = N_0 e^{-kt}$$

$$ln\frac{N}{N_0} = -kt$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the *half-life of the isotope*. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.5.1, along with some of their applications.

**Table 14.5.1 Half-Lives and Applications of Some Radioactive Isotopes**

| Radioactive Isotope | Half-Life | Typical Uses |
|---|---|---|
| hydrogen-3 (tritium) | 12.32 yr | biochemical tracer |
| carbon-11 | 20.33 min | positron emission tomography (biomedical imaging) |
| carbon-14 | $5.70 \times 10^3$ yr | dating of artifacts |
| sodium-24 | 14.951 h | cardiovascular system tracer |
| phosphorus-32 | 14.26 days | biochemical tracer |
| potassium-40 | $1.248 \times 10^9$ yr | dating of rocks |
| iron-59 | 44.495 days | red blood cell lifetime tracer |
| cobalt-60 | 5.2712 yr | radiation therapy for cancer |
| technetium-99*m** | 6.006 h | biomedical imaging |
| iodine-131 | 8.0207 days | thyroid studies tracer |
| radium-226 | $1.600 \times 10^3$ yr | radiation therapy for cancer |
| uranium-238 | $4.468 \times 10^9$ yr | dating of rocks and Earth's crust |
| americium-241 | 432.2 yr | smoke detectors |

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

### Note the Pattern

Radioactive decay is a first-order process.

## Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as *radioisotope dating* techniques.

The most common method for measuring the age of ancient objects is *carbon-14 dating*. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the $CO_2$ that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as *beta decay*, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}C \rightarrow ^{14}N + \beta^-$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is $1.3 \times 10^{-12}$, with a decay rate of 15 dpm/g of carbon (Figure 14.18). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11.Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

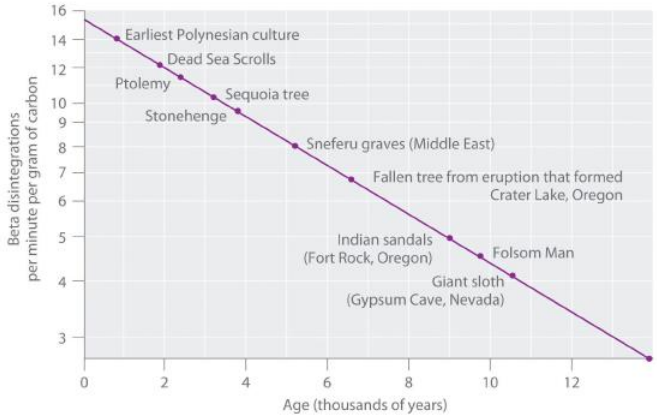



Figure 14.5.2 Radiocarbon **Dating**A plot of the specific activity of $^{14}C$ versus age for a number of archaeological samples shows an inverse linear relationship between $^{14}C$ content (a log scale) and age (a linear scale).

## Example 14.5.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the $^{14}C$ content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

**Given:** isotope and final activity

**Asked for:** elapsed time

**Strategy:**

**A** Use Equation 14.5.5 to calculate $N_0/N$. Then substitute the value for the half-life of $^{14}C$ into Equation 14.5.3 to find the rate constant for the reaction.

**B** Using the values obtained for $N_0/N$ and the rate constant, solve Equation 14.5.7 to obtain the elapsed time.

**Solution:**

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 14.5.7) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$ln\frac{N}{N_0} = -kt$$

$$\frac{ln\,(N_0/N)}{k} = t$$

**A** From Equation 14.5.5, we know that $A = kN$. We can therefore use the initial and final activities ($A_0$ = 15 dpm and $A$ = 8.0 dpm) to calculate $N_0/N$:

$$\frac{A_0}{A} = \frac{\cancel{k}\,N_0}{\cancel{k}\,N} = \frac{N_0}{N} = \frac{15.}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 14.5.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ yr} = 1.22 \times 10^{-4}\ yr^{-1}$$

**B** Substituting into the equation for $t$,

$$t = \frac{ln\,(N_0/N)}{k} = \frac{ln\,(15./8.0)}{1.22 \times 10^{-4}\ yr^{-1}} = 5.2 \times 10^{3}\ yr$$

From our calculations, the man died 5200 yr ago.

Exercise

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a $^{14}C$ decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

**Answer:** 30,000 yr

## Summary

The **half-life** of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$.

Radioactive decay reactions are first-order reactions. The **rate of decay**, or **activity**, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

## Key Takeaways

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

## Key Equations

**half-life of first-order reaction**

Equation 14.5.3 $t_{1/2} = \dfrac{0.693}{k}$

**radioactive decay**

Equation 14.5.5: $A = kN$

## Conceptual Problems

1. What do chemists mean by the *half-life* of a reaction?
2. If a sample of one isotope undergoes more disintegrations per second than the same number of atoms of another isotope, how do their half-lives compare?

## Numerical Problems

1. Half-lives for the reaction A + B → C were calculated at three values of $[A]_0$, and [B] was the same in all cases. The data are listed in the following table:

| $[A]_0$ (M) | $t_{½}$ (s) |
|---|---|
| 0.50 | 420 |
| 0.75 | 280 |
| 1.0 | 210 |

   Does this reaction follow first-order kinetics? On what do you base your answer?

2. Ethyl-2-nitrobenzoate ($NO_2C_6H_4CO_2C_2H_5$) hydrolyzes under basic conditions. A plot of $[NO_2C_6H_4CO_2C_2H_5]$ versus $t$ was used to calculate $t_{½}$, with the following results:

| $[NO_2C_6H_4CO_2C_2H_5]$ ($M/cm^3$) | $t_{½}$ (s) |
|---|---|
| 0.050 | 240 |
| 0.040 | 300 |
| 0.030 | 400 |

Is this a first-order reaction? Explain your reasoning.

3. Azomethane ($CH_3N_2CH_3$) decomposes at 600 K to $C_2H_6$ and $N_2$. The decomposition is first order in azomethane. Calculate $t_{½}$ from the data in the following table:

| Time (s) | $P_{Azomethane}$ (atm) |
|---|---|
| 0 | $8.2 \times 10^{-2}$ |
| 2000 | $3.99 \times 10^{-2}$ |
| 4000 | $1.94 \times 10^{-2}$ |

How long will it take for the decomposition to be 99.9% complete?

4. The first-order decomposition of hydrogen peroxide has a half-life of 10.7 h at 20°C. What is the rate constant (expressed in $s^{-1}$) for this reaction? If you started with a solution that was $7.5 \times 10^{-3}$ M $H_2O_2$, what would be the initial rate of decomposition (M/s)? What would be the concentration of $H_2O_2$ after 3.3 h?

## Answers

1. No; the reaction is second order in A because the half-life decreases with increasing reactant concentration according to $t_{1/2} = 1/k[A_0]$.
2. 
3. $t_{1/2} = 1.92 \times 10^3$ s or 1920 s; 19100 s or 5.32 hrs.
4. 

## Contributors

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# 14.7: Reaction Rates - A Microscopic View

**Learning Objectives**

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the *mechanism* of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the **reaction mechanism**.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2C_8H_{18}\,(l) + 25O_2\,(g) \rightarrow 16CO_2\,(g) + 18H_2O\,(g)$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an elementary reactionEach of the complex series of reactions that take place in a stepwise fashion to convert reactants to products., involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the mechanism of the reaction. *The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.*

## Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of $NO_2$ with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k\,[NO_2]^2$$

The fact that the reaction is second order in [$NO_2$] and independent of [CO] tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be rate = $k$[$NO_2$][CO].

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

$$\begin{array}{lll} step\ 1 & NO_2 + NO_2 \overset{slow}{\rightarrow} NO_3 + NO & elementary\ reaction \\ step\ 2 & \underline{NO_3 + CO \rightarrow NO_2 + CO_2} & elementary\ reaction \\ sum & NO_2 + CO \rightarrow NO + CO_2 & overall reaction \end{array}$$

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The $NO_3$ molecule is an intermediateA species in a reaction mechanism that does not appear in the balanced chemical equation for the overall reaction. in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

### Note the Pattern

The sum of the elementary reactions in a reaction mechanism must give the overall balanced chemical equation of the reaction.

## Using Molecularity to Describe a Rate Law

The molecularityThe number of molecules that collide during any step in a reaction mechanism. of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as *unimolecular*; if there are two reactant molecules, it is *bimolecular*; and if there are three

reactant molecules (a relatively rare situation), it is *termolecular*. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order *of the elementary reaction* is the same as its molecularity (Table 14.6.1 ). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is rate = $k$[A]. For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 14.6.1 For a bimolecular elementary reaction of the form A + B → products, the general rate law is rate = $k$[A][B].

**Table 14.6.1 Common Types of Elementary Reactions and Their Rate Laws**

| Elementary Reaction | Molecularity | Rate Law | Reaction Order |
|---|---|---|---|
| A → products | unimolecular | rate = $k$[A] | first |
| 2A → products | bimolecular | rate = $k$[A]$^2$ | second |
| A + B → products | bimolecular | rate = $k$[A][B] | second |
| 2A + B → products | termolecular | rate = $k$[A]$^2$[B] | third |
| A + B + C → products | termolecular | rate = $k$[A][B][C] | third |

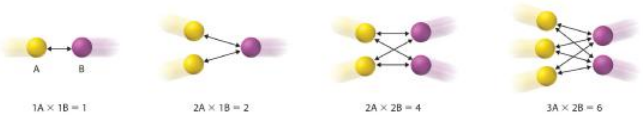



Figure 14.6.1 The Basis for Writing Rate Laws of Elementary **Reactions** This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the *product* of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step.

## Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we *cannot* obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the *slowest* overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the rate-determining stepThe slowest step in a reaction mechanism., that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



**Rate-determining step.** The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow.

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

$$step\ 1 \quad NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \qquad rate = k_1\,[NO_2]^2\ predicted$$

$$step\ 2 \quad \underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2} \qquad rate = k_2\,[NO_3]\,[CO_2]\ predicted$$

$$sum \quad NO_2 + CO \xrightarrow{k} NO + CO_2 \qquad rate = k\,[NO_2]^2\ observed$$

The experimentally determined rate law for the reaction of $NO_2$ with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so $k$ for the overall reaction must equal $k_1$. That is, $NO_3$ is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

### Example 14.6.1

In an alternative mechanism for the reaction of $NO_2$ with CO, $N_2O_4$ appears as an intermediate.

$$step\ 1 \qquad NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$$

$$step\ 2 \quad \underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$$

$$sum \qquad NO_2 + CO \rightarrow NO + CO_2$$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

**Given:** elementary reactions

**Asked for:** rate law for each elementary reaction and overall rate law

**Strategy:**

**A** Determine the rate law for each elementary reaction in the reaction.

**B** Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

**Solution:**

**A** The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

**B** If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with $N_2O_4$ as an intermediate, and the one described previously, with $NO_3$ as an intermediate, are kinetically indistinguishable. In this case, further experiments are

needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, $NO_3$ and $N_2O_4$, directly.

Exercise A

Iodine monochloride (ICl) reacts with $H_2$ as follows:

$$2ICl\,(g) + H_2\,(g) \rightarrow HCl\,(g) + I_2\,(s)$$

The experimentally determined rate law is rate = $k$[ICl][$H_2$]. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

**Answer**

$$step\ 1 \quad ICl + H_2 \xrightarrow{k_1} HCl + HI \quad rate = k_1\,[ICl]\,[H_2]\ slow$$

$$step\ 2 \quad \underline{HI + ICl \xrightarrow{k_2} HCl + I_2} \quad rate = k_2\,[HI]\,[ICl]\ fast$$

$$sum \quad 2ICl + H_2 \rightarrow 2HCl + I_2$$

This mechanism is consistent with the experimental rate law *if* the first step is the rate-determining step.

Exercise B

The reaction between NO and $H_2$ occurs via a three-step process:

$$step\ 1 \quad NO + NO \xrightarrow{k_1} N_2O_2 + NO \quad fast$$

$$step\ 2 \quad N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \quad slow$$

$$step3 \quad N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O \quad fast$$

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: rate = $k$[NO]$^2$[$H_2$]$^2$?

**Answer**

- rate = $k_1$[NO]$^2$;
- rate = $k_2$[$N_2O_2$][$H_2$];
- rate = $k_3$[$N_2O$][$H_2$];
- 2NO(g) + 2$H_2$(g) → $N_2$(g) + 2$H_2O$(g)
- step 2
- Yes, because the rate of formation of [$N_2O_2$] = $k_1$[NO]$^2$. Substituting $k_1$[NO]$^2$ for [$N_2O_2$] in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

## Chain Reactions

Many reaction mechanisms, like those discussed so far, consist of only two or three elementary reactions. Many others consist of long series of elementary reactions. The most common mechanisms are chain reactionsA reaction mechanism in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process., in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process. Chain reactions occur in fuel combustion, explosions, the formation of many polymers, and the tissue changes associated with aging. They are also important in the chemistry of the atmosphere.

Chain reactions are described as having three stages. The first is *initiation*, a step that produces one or more reactive intermediates. Often these intermediates are radicalsSpecies that have one or more unpaired valence electrons., species that have an unpaired valence electron. In the second stage, *propagation*, reactive intermediates are continuously consumed and regenerated while products are formed. Intermediates are also consumed but not regenerated in the final stage of a chain reaction, *termination*, usually by forming stable products.

Let us look at the reaction of methane with chlorine at elevated temperatures (400°C–450°C), a chain reaction used in industry to manufacture methyl chloride ($CH_3Cl$), dichloromethane ($CH_2Cl_2$), chloroform ($CHCl_3$), and carbon tetrachloride ($CCl_4$):

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

Direct chlorination generally produces a mixture of all four carbon-containing products, which must then be separated by distillation. In our discussion, we will examine only the chain reactions that lead to the preparation of $CH_3Cl$.

In the initiation stage of this reaction, the relatively weak Cl–Cl bond cleaves at temperatures of about 400°C to produce chlorine atoms (Cl·):

$$Cl_2 \rightarrow 2Cl\cdot$$

During propagation, a chlorine atom removes a hydrogen atom from a methane molecule to give HCl and $CH_3$·, the methyl radical:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The methyl radical then reacts with a chlorine molecule to form methyl chloride and another chlorine atom, Cl·:

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

The sum of the propagation reactions is the same as the overall balanced chemical equation for the reaction:

$$\begin{array}{l} \cancel{Cl\cdot} + CH_4 \rightarrow \cancel{CH_3\cdot} + HCl \\ \cancel{CH_3\cdot} + Cl_2 \rightarrow CH_3Cl + \cancel{Cl\cdot} \\ \hline Cl_2 + CH_4 \rightarrow CH_3Cl + HCl \end{array}$$

Without a chain-terminating reaction, propagation reactions would continue until either the methane or the chlorine was consumed. Because radical species react rapidly with almost anything, however, including each other, they eventually form neutral compounds, thus terminating the chain reaction in any of three ways:

\(

$$\begin{array}{c} CH_3\cdot + Cl\cdot \rightarrow CH_3Cl \\ CH_3\cdot + CH_3\cdot \rightarrow H_3CCH_3 \\ Cl\cdot + Cl\cdot \rightarrow Cl_2 \end{array} \qquad (14.7.1)$$

Here is the overall chain reaction, with the desired product ($CH_3Cl$) in bold:

| | |
|---|---|
| *Initiation*: | $Cl_2$ → 2Cl· |
| *Propagation*: | Cl· + $CH_4$ → $CH_3$· + HCl |
| | $CH_3$· + $Cl_2$ → **$CH_3Cl$** + Cl· |
| *Termination*: | $CH_3$· + Cl· → **$CH_3Cl$** |
| | $CH_3$· + $CH_3$· → $H_3CCH_3$ |
| | Cl· + Cl· → $Cl_2$ |

The chain reactions responsible for explosions generally have an additional feature: the existence of one or more *chain branching steps*, in which one radical reacts to produce two or more radicals, each of which can then go on to start a new chain reaction. Repetition of the branching step has a cascade effect such that a single initiation step generates large numbers of chain reactions. The result is a very rapid reaction or an explosion.

The reaction of $H_2$ and $O_2$, used to propel rockets, is an example of a chain branching reaction:

| | |
|---|---|
| *Initiation*: | $H_2 + O_2 \rightarrow HO_2\cdot + H\cdot$ |
| *Propagation*: | $HO_2\cdot + H_2 \rightarrow H_2O + OH\cdot$ |
| | $OH\cdot + H_2 \rightarrow H_2O + H\cdot$ |
| *Termination*: | $H\cdot + O_2 \rightarrow OH\cdot + \cdot O\cdot$ |
| | $\cdot O\cdot + H_2 \rightarrow OH\cdot + H\cdot$ |

Termination reactions occur when the extraordinarily reactive H· or OH· radicals react with a third species. The complexity of a chain reaction makes it unfeasible to write a rate law for the overall reaction.

## Summary

A **reaction mechanism** is the microscopic path by which reactants are transformed into products. Each step is an **elementary reaction**. Species that are formed in one step and consumed in another are **intermediates**. Each elementary reaction can be described in terms of its **molecularity**, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the **rate-determining step**. **Chain reactions** consist of three kinds of reactions: initiation, propagation, and termination. Intermediates in chain reactions are often **radicals**, species that have an unpaired valence electron.

## Key Takeaway

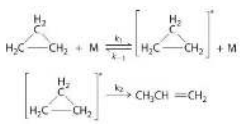
- A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law.

## Conceptual Problems

1. How does the term *molecularity* relate to elementary reactions? How does it relate to the overall balanced chemical equation?
2. What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?
3. When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?
4. If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?
5. Give the rate-determining step for each case.
    1. Traffic is backed up on a highway because two lanes merge into one.
    2. Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
    3. A document containing text and graphics is downloaded from the Internet.
6. Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

## Numerical Problems

1. Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



    where M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

2. Above approximately 500 K, the reaction between $NO_2$ and CO to produce $CO_2$ and NO follows the second-order rate law $\Delta[CO_2]/\Delta t = k[NO_2][CO]$. At lower temperatures, however, the rate law is $\Delta[CO_2]/\Delta t = k'[NO_2]^2$, for which it is known that $NO_3$ is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?
3. Nitramide ($O_2NNH_2$) decomposes in aqueous solution to $N_2O$ and $H_2O$. What is the experimental rate law ($\Delta[N_2O]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?

$$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightarrow}} O_2NNH^- + H^+ \quad fast$$

$$O_2NNH^- \overset{k_2}{\rightarrow} N_2O + OH^- \quad slow$$

$$H^+ + OH^- \overset{k_3}{\rightarrow} H_2O \quad fast$$

Assume that the rates of the forward and reverse reactions in the first equation are equal.

4. The following reactions are given:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightarrow}} C + D$$

$$D + E \overset{k_2}{\rightarrow} F$$

What is the relationship between the relative magnitudes of $k_{-1}$ and $k_2$ if these reactions have the rate law $\Delta[F]/\Delta t = k[A][B][E]/[C]$? How does the magnitude of $k_1$ compare to that of $k_2$? Under what conditions would you expect the rate law to be $\Delta[F]/\Delta t = k'[A][B]$? Assume that the rates of the forward and reverse reactions in the first equation are equal.

## Answers

1. The $k_2$ step is likely to be rate limiting; the rate cannot proceed any faster than the second step.
2. 
3. $rate = k_2 \dfrac{k_1 [O_2NNH_2]}{k_{-1}[H^+]} = k\dfrac{[O_2NNH_2]}{[H^+]}$
4. 

## Contributors

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Modified by Joshua B. Halpern

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# 14.8: The Collision Model of Chemical Kinetics

**Learning Objectives**

- To understand why and how chemical reactions occur.

In Section 14.6 , you saw that it is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the *collision model of chemical kinetics*, which is a useful tool for understanding the behavior of reacting chemical species. According to the collision model, a chemical reaction can occur only when the reactant molecules, atoms, or ions collide with more than a certain amount of kinetic energy and in the proper orientation. The collision model explains why, for example, most collisions between molecules do *not* result in a chemical reaction. Nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about $10^{30}$ times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then $NO_2$ a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide. The collision model also explains why such chemical reactions occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates.

## Activation Energy

In Chapter 10 we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of activation energy ($E_a$)The energy barrier or threshold that corresponds to the minimum amount of energy the particles in a reaction must have to react when they colllide.. We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

The reaction rate, not the rate constant, will vary with concentration. The rate constant, however, does vary with temperature. Figure 14..7.1 shows a plot of the rate constant of the reaction of NO with $O_3$ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (Chapter 11) and of conductivity versus temperature (Chapter 12). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

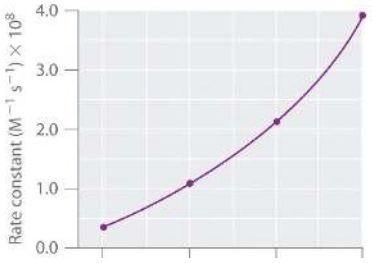


**Figure 14.7.1 Rate Constant versus Temperature for the Reaction of NO with $O_3$** The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases.

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the activation energy, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the activated complexAlso called the transition state, the arrangement of atoms that first forms when molecules are able to overcome the activation energy and react. or the transition stateAlso called the activated complex, the arrangement of atoms that first forms when molecules are able to overcome the activation energy and react. of the reaction. The activated complex is *not* a reaction intermediate; it does not last long enough to be detected readily.

### Note the Pattern

Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.

## Graphing Energy Changes during a Reaction

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 14.7.2 shows a plot for the NO–$O_3$ system, in which the vertical axis is potential energy and the horizontal axis is the *reaction coordinate*, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction ($\Delta E$) is negative, which means that the reaction releases energy. (In this case, $\Delta E$ is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction ($E_a$ is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

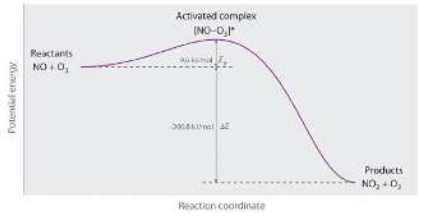



Figure 14.7.2 Energy of the Activated Complex for the NO–$O_3$ **System** The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex.

Part (a) in Figure 14.7.3 illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, part (b) in Figure 14.22 illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta E > 0$. Although the energy changes that result from a reaction can be positive, negative, or even zero, in all cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is always positive.

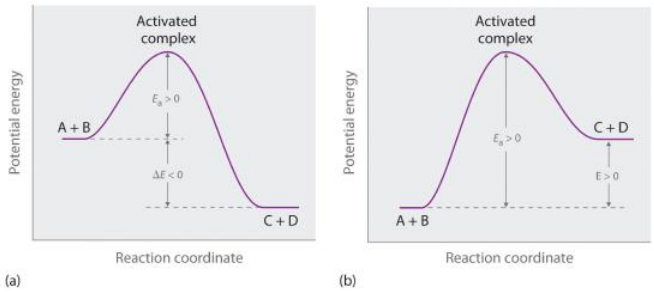



Figure 14.7.3 Differentiating between $E_a$ and $\Delta E$ The potential energy diagrams for a reaction with (a) $\Delta E < 0$ and (b) $\Delta E > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. $E_a$ is always positive. For a reaction such as the one shown in (b), $E_a$ must be *greater* than $\Delta E$.

### Note the Pattern

For similar reactions under comparable conditions, the one with the smallest $E_a$ will occur most rapidly.

Whereas $\Delta E$ is related to the tendency of a reaction to occur spontaneously, $E_a$ gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. (For more information on spontaneous reactions, see Chapter 18.) *For two similar reactions under comparable conditions, the reaction with the smallest $E_a$ will occur more rapidly.*

Even when the energy of collisions between two reactant species is greater than $E_a$, however, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and $O_3$ to produce $NO_2$ and $O_2$, a terminal oxygen atom of $O_3$ must collide with the nitrogen atom of NO at an angle that allows $O_3$ to transfer an oxygen atom to NO to produce $NO_2$ (Figure 14.7.4. All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and $O_3$ result in a reaction at kinetic energies greater than $E_a$, most collisions of NO and $O_3$ are unproductive. The fraction of orientations that result in a reaction is called the steric factor ($p$)The fraction of orientations of particles that result in a chemical reaction., and, in general, its value can range from 0 (no orientations of molecules result in reaction) to 1 (all orientations result in reaction).

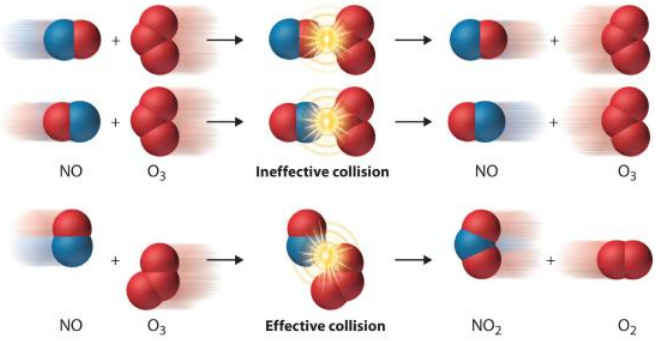



Figure 14.7.4 The Effect of Molecular Orientation on the Reaction of NO and $O_3$ Most collisions of NO and $O_3$ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of $O_3$ are likely to produce $NO_2$ and $O_2$, even if the molecules collide with $E > E_a$.

## The Arrhenius Equation

Figure 14.7.5 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than $E_a$; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than $E_a$. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

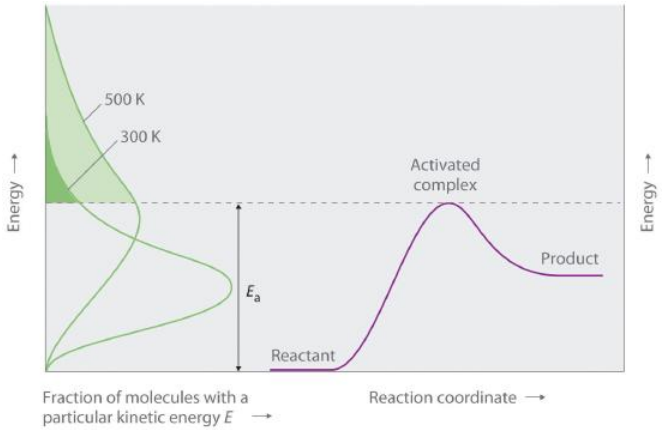



Figure 14.7.5 Surmounting the Energy Barrier to a Reaction This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have $E > E_a$ and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K.

For an A + B elementary reaction, all the factors that affect the reaction rate can be summarized in a single series of relationships:

rate = (collision frequency)(steric factor)(fraction of collisions with $E > E_a$)

where

$$rate = k\,[A]\,[B]$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, *A*, called the frequency factorA constant in the Arrhenius equation, it converts concentrations to collisions per second.:

$$k = Ae^{-E_a/RT}$$

The frequency factor is used to convert concentrations to collisions per second.Because the frequency of collisions depends on the temperature, *A* is actually *not* constant. Instead, *A* increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time. Equation 14.39 is known as the Arrhenius equationAn expression that summarizes the collision model of chemical kinetics: k= Aexp($E_a$/RT) and summarizes the collision model of chemical kinetics, where *T* is the absolute temperature (in K) and *R* is the ideal gas constant [8.314 J/(K·mol)]. $E_a$ indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large $E_a$ increases rapidly with increasing temperature, whereas the reaction rate with a smaller $E_a$ increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 14.7.3,

$$ln\ k = ln\ A - \frac{E_a}{RT} = ln\ A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right]$$

Equation 14.40 is the equation of a straight line, $y = mx + b$, where $y = \ln k$ and $x = 1/T$. This means that a plot of ln *k* versus 1/*T* is a straight line with a slope of $-E_a/R$ and an intercept of ln *A*. In fact, we need to measure the reaction rate at only two temperatures to estimate $E_a$.

Knowing the $E_a$ at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining $E_a$ from reaction rates measured at several temperatures is illustrated in Example 13.

### Example 14.7.1

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (*f*) as a function of temperature (*T*). Use the data in the following table, along with the graph of ln[chirping rate] versus 1/*T* in Figure 14.7.6 to calculate $E_a$ for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

| Frequency ($f$; chirps/min) | ln $f$ | $T$ (K) | 1/$T$ (K) |
|---|---|---|---|
| 200 | 5.30 | 299 | $3.34 \times 10^{-3}$ |
| 179 | 5.19 | 298 | $3.36 \times 10^{-3}$ |
| 158 | 5.06 | 296 | $3.38 \times 10^{-3}$ |
| 141 | 4.95 | 294 | $3.40 \times 10^{-3}$ |
| 126 | 4.84 | 293 | $3.41 \times 10^{-3}$ |
| 112 | 4.72 | 292 | $3.42 \times 10^{-3}$ |
| 100 | 4.61 | 290 | $3.45 \times 10^{-3}$ |
| 89 | 4.49 | 289 | $3.46 \times 10^{-3}$ |
| 79 | 4.37 | 287 | $3.48 \times 10^{-3}$ |

**Given:** chirping rate at various temperatures

**Asked for:** activation energy and chirping rate at specified temperature

**Strategy:**

**A** From the plot of ln $f$ versus 1/$T$ in Figure 14.7.6, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.

**B** Express Equation 14.7.4 in terms of $k_1$ and $T_1$ and then in terms of $k_2$ and $T_2$.

**C** Subtract the two equations; rearrange the result to describe $k_2/k_1$ in terms of $T_2$ and $T_1$.

**D** Using measured data from the table, solve the equation to obtain the ratio $k_2/k_1$. Using the value listed in the table for $k_1$, solve for $k_2$.

**Solution:**

**A** If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of ln $f$ versus 1/$T$ should give a straight line (Figure 14.7.6 ). Also, the slope of the plot of ln $f$ versus 1/$T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 14.7.6 to estimate the slope:

$$slope = \frac{\Delta\ ln\ f}{\Delta\ (1/T)} = \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ K^{-1} - 3.48 \times 10^{-3}\ K^{-1}}$$

A computer best-fit line through all the points has a slope of $-6.67 \times 10^3$ K, so our estimate is very close. We now use it to solve for the activation energy:

$$E_a = \frac{0.93}{-0.041 \times 10^{-3}\ K^{-1}} = 6.6 \times 10^3\ K$$

**B** If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 14.40 to express the known rate constant ($k_1$) at the first temperature ($T_1$) as follows:

$$ln\ k_1 = ln\ A - \frac{E_a}{RT_1}$$

Similarly, we can express the unknown rate constant ($k_2$) at the second temperature ($T_2$) as follows:

$$ln\ k_2 = ln\ A - \frac{E_a}{RT_2}$$

**C** These two equations contain four known quantities ($E_a$, $T_1$, $T_2$, and $k_1$) and two unknowns ($A$ and $k_2$). We can eliminate $A$ by subtracting the first equation from the second:

$$ln\ k_2 - ln\ k_1 = \left(ln\ A - \frac{E_a}{RT_2}\right) - \left(ln\ A - \frac{E_a}{RT_1}\right) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

Then

$$ln\ \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

**D** To obtain the best prediction of chirping rate at 308 K ($T_2$), we try to choose for $T_1$ and $k_1$ the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for $T_1$ = 296 K, where $f$ = 158, and using the $E_a$ calculated previously,

$$ln\ \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{55\ kJ/mol}{8.314\ J/(K \cdot mol)}\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1}{296\ K} - \frac{1}{308\ K}\right) = 0.87$$

Thus $k_{308}/k_{296}$ = 2.4 and $k_{308}$ = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

Exercise

The equation for the decomposition of $NO_2$ to NO and $O_2$ is second order in $NO_2$:

$$2NO_2\,(g) \rightarrow 2NO\,(g) + O_2\,(g)$$

Data for the reaction rate as a function of temperature are listed in the following table. Calculate $E_a$ for the reaction and the rate constant at 700 K.

| $T$ (K) | $k$ ($M^{-1}{\cdot}s^{-1}$) |
|---|---|
| 592 | 522 |
| 603 | 755 |
| 627 | 1700 |
| 652 | 4020 |
| 656 | 5030 |

**Answer:** $E_a$ = 114 kJ/mol; $k_{700}$ = 18,600 $M^{-1}{\cdot}s^{-1}$ = 1.86 × $10^4$ $M^{-1}{\cdot}s^{-1}$.

What $E_a$ results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

**Answer:** about 51 kJ/mol

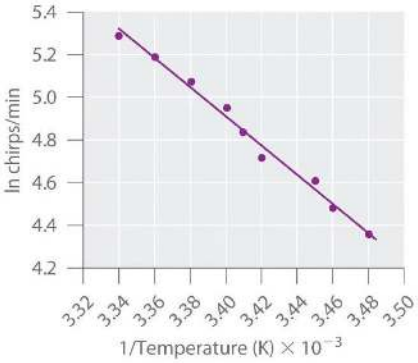



Figure 14.7.6 Graphical Determination of $E_a$ for Tree Cricket Chirping When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/$T$, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an $E_a$ of 55 kJ/mol.

## Summary

A minimum energy (**activation energy,** $E_a$) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the **activated complex**, or **transition state**, of the reaction. At a given temperature, the higher the $E_a$, the slower the reaction. The fraction of orientations that result in a reaction is the **steric factor**. The **frequency factor**, steric factor, and activation energy are related to the rate constant in the **Arrhenius equation**: k = Aexp(-$E_a$/RT). A plot of the natural logarithm of $k$ versus 1/$T$ is a straight line with a slope of $-E_a/R$.

## Key Takeaway

- For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation.

## Key Equation

**Arrhenius equation**

$k = Ae^{-E_a/RT}$

## Conceptual Problems

1. Although an increase in temperature results in an increase in kinetic energy, this increase in kinetic energy is not sufficient to explain the relationship between temperature and reaction rates. How does the activation energy relate to the chemical kinetics of a reaction? Why does an increase in temperature increase the reaction rate despite the fact that the average kinetic energy is still less than the activation energy?
2. For any given reaction, what is the relationship between the activation energy and each of the following?
    1. electrostatic repulsions
    2. bond formation in the activated complex
    3. the nature of the activated complex
3. If you are concerned with whether a reaction will occur rapidly, why would you be more interested in knowing the magnitude of the activation energy than the change in potential energy for the reaction?
4. The product C in the reaction A + B → C + D can be separated easily from the reaction mixture. You have been given pure A and pure B and are told to determine the activation energy for this reaction to determine whether the reaction is suitable for the industrial synthesis of C. How would you do this? Why do you need to know the magnitude of the activation energy to make a decision about feasibility?
5. Above $E_a$, molecules collide with enough energy to overcome the energy barrier for a reaction. Is it possible for a reaction to occur at a temperature less than that needed to reach $E_a$? Explain your answer.
6. What is the relationship between $A$, $E_a$, and $T$? How does an increase in $A$ affect the reaction rate?
7. Of two highly exothermic reactions with different values of $E_a$, which would need to be monitored more carefully: the one with the smaller value or the one with the higher value? Why?

## Numerical Problems

1. What happens to the approximate rate of a reaction when the temperature of the reaction is increased from 20°C to 30°C? What happens to the reaction rate when the temperature is raised to 70°C? For a given reaction at room temperature (20°C), what is the shape of a plot of reaction rate versus temperature as the temperature is increased to 70°C?
2. Acetaldehyde, used in silvering mirrors and some perfumes, undergoes a second-order decomposition between 700 and 840 K. From the data in the following table, would you say that acetaldehyde follows the general rule that each 10 K increase in temperature doubles the reaction rate?

| $T$ (K) | $k$ ($M^{-1}·s^{-1}$) |
|---|---|
| 720 | 0.024 |
| 740 | 0.051 |
| 760 | 0.105 |
| 800 | 0.519 |

3. Bromoethane reacts with hydroxide ion in water to produce ethanol. The activation energy for this reaction is 90 kJ/mol. If the reaction rate is $3.6 \times 10^{-5}$ M/s at 25°C, what would the reaction rate be at the following temperatures?

1. 15°C
2. 30°C
3. 45°C

4. An enzyme-catalyzed reaction has an activation energy of 15 kcal/mol. How would the value of the rate constant differ between 20°C and 30°C? If the enzyme reduced the $E_a$ from 25 kcal/mol to 15 kcal/mol, by what factor has the enzyme increased the reaction rate at each temperature?

5. The data in the following table are the rate constants as a function of temperature for the dimerization of 1,3-butadiene. What is the activation energy for this reaction?

| $T$ (K) | $k$ ($M^{-1}·min^{-1}$) |
|---|---|
| 529 | 1.4 |
| 560 | 3.7 |
| 600 | 25 |
| 645 | 82 |

6. The reaction rate at 25°C is $1.0 \times 10^{-4}$ M/s. Increasing the temperature to 75°C causes the reaction rate to increase to $7.0 \times 10^{-2}$ M/s. Estimate $E_a$ for this process. If $E_a$ were 25 kJ/mol and the reaction rate at 25°C is $1.0 \times 10^{-4}$ M/s, what would be the reaction rate at 75°C?

## Answers

1. The reaction rate will approximately double: 20°C to 30°C, the reaction rate increases by about $2^1 = 2$; 20°C to 70°C, the reaction rate increases by about $2^5 = 32$-fold. A plot of reaction rate versus temperature will give an exponential increase: rate $\propto 2^{\Delta T/10}$.
2. 
3. 
   1. $1.0 \times 10^{-5}$ M/s
   2. $6.6 \times 10^{-5}$ M/s
   3. $3.5 \times 10^{-4}$ M/s
4. 
5. 100 kJ/mol
6. 

## Contributors

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# 14.9: Catalysis

**Learning Objectives**

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Chapter 7 described catalysts A substance that participates in a reaction and causes it to occur more rapidly but that can be recovered unchanged at the end of the reaction and reused. Catalysts may also control which products are formed in a reaction. as substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it *must* appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower $E_a$, but the *net* change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is *not* affected by the presence of a catalyst (Figure 14.8.1 ). Nevertheless, because of its lower $E_a$, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of *both* the forward *and* the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, **homogeneous catalysts**, and **enzymes**.

### Note the Pattern

A catalyst affects $E_a$, not $\Delta E$.

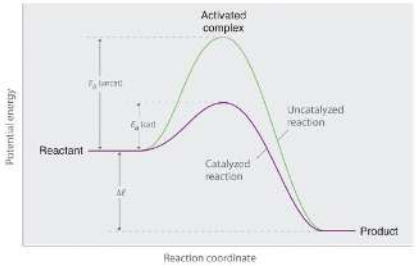



Figure 14.8.1 Lowering the Activation Energy of a Reaction by a **Catalyst** This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect $\Delta E$).

## Heterogeneous Catalysis

In heterogeneous catalysisA catalytic reaction in which the catalyst is in a different phase from the reactants., the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called *adsorption* in such a way that a chemical bond in the reactant becomes weak and then breaks. *Poisons* are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 14.8.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called *desorption*. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of $H_2$ is substantially lower on the catalyst surface.

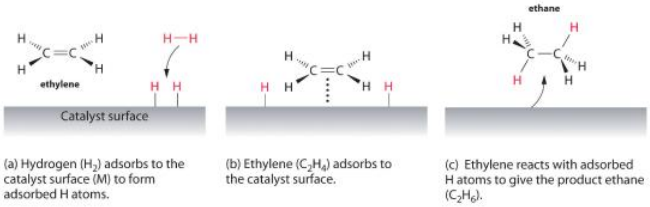



Figure 14.8.2 Hydrogenation of Ethylene on a Heterogeneous Catalyst When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous $H_2$. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released.

Figure 14.8.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 14.8.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

**Table 14.8.1 Some Commercially Important Reactions that Employ Heterogeneous Catalysts**

| Commercial Process | Catalyst | Initial Reaction | Final Commercial Product |
|---|---|---|---|
| contact process | $V_2O_5$ or Pt | $2SO_2 + O_2 \rightarrow 2SO_3$ | $H_2SO_4$ |
| Haber process | Fe, $K_2O$, $Al_2O_3$ | $N_2 + 3H_2 \rightarrow 2NH_3$ | $NH_3$ |
| Ostwald process | Pt and Rh | $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ | $HNO_3$ |
| water–gas shift reaction | Fe, $Cr_2O_3$, or Cu | $CO + H_2O \rightarrow CO_2 + H_2$ | $H_2$ for $NH_3$, $CH_3OH$, and other fuels |
| steam reforming | Ni | $CH_4 + H_2O \rightarrow CO + 3H_2$ | $H_2$ |
| methanol synthesis | ZnO and $Cr_2O_3$ | $CO + 2H_2 \rightarrow CH_3OH$ | $CH_3OH$ |
| Sohio process | bismuth phosphomolybdate | $CH_2{=}CHCH_3 + NH_3 + 3/2O_2 \rightarrow CH_2{=}CHCN + 3H_2O$ | $CH_2{=}CHCN$ |
| catalytic hydrogenation | Ni, Pd, or Pt | $RCH{=}CHR' + H_2 \rightarrow RCH_2{-}CH_2R'$ | partially hydrogenated oils for margarine, and so forth |

## Homogeneous Catalysis

In homogeneous catalysisA catalytic reaction in which the catalyst is uniformly dispersed throughout the reactant mixture to form a solution., the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 14.8.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

**Table 14.8.2 Some Commercially Important Reactions that Employ Homogeneous Catalysts**

| Commercial Process | Catalyst | Reactants | Final Product |
|---|---|---|---|
| Union Carbide | $[Rh(CO)_2I_2]^-$ | $CO + CH_3OH$ | $CH_3CO_2H$ |
| hydroperoxide process | Mo(VI) complexes | $CH_3CH=CH_2$ + R–O–O–H |  |
| hydroformylation | $Rh/PR_3$ complexes | $RCH=CH_2 + CO + H_2$ | $RCH_2CH_2CHO$ |
| adiponitrile process | $Ni/PR_3$ complexes | $2HCN + CH_2=CHCH=CH_2$ | $NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon |
| olefin polymerization | $(RC_5H_5)_2ZrCl_2$ | $CH_2=CH_2$ | $–(CH_2CH_2–)_n$: high-density polyethylene |

## Enzymes

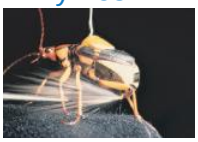


**Figure 14.8.3 A Catalytic Defense Mechanism** The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of $H_2O_2$.

**Enzymes**, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a substrateThe reactant in an enzyme-catalyzed reaction..

Because enzymes can increase reaction rates by enormous factors (up to $10^{17}$ times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37°C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be *proteases*, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 14.8.3).

Enzyme inhibitorsSubstances that decrease the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of the enzyme, thus slowing or preventing a reaction from occurring. cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

## Summary

**Catalysts** participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In **heterogeneous catalysis**, catalysts provide a surface to which reactants bind in a process of adsorption. In **homogeneous catalysis**, catalysts are in the same phase as the reactants. **Enzymes** are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a **substrate**. **Enzyme inhibitors** cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

## Key Takeaway

- Catalysts allow a reaction to proceed via a pathway that has a lower activation energy.

## Conceptual Problems

1. What effect does a catalyst have on the activation energy of a reaction? What effect does it have on the frequency factor ($A$)? What effect does it have on the change in potential energy for the reaction?
2. How is it possible to affect the product distribution of a reaction by using a catalyst?
3. A heterogeneous catalyst works by interacting with a reactant in a process called *adsorption*. What occurs during this process? Explain how this can lower the activation energy.
4. What effect does increasing the surface area of a heterogeneous catalyst have on a reaction? Does increasing the surface area affect the activation energy? Explain your answer.
5. Identify the differences between a heterogeneous catalyst and a homogeneous catalyst in terms of the following.
    1. ease of recovery
    2. collision frequency
    3. temperature sensitivity
    4. cost
6. An area of intensive chemical research involves the development of homogeneous catalysts, even though homogeneous catalysts generally have a number of operational difficulties. Propose one or two reasons why a homogenous catalyst may be preferred.
7. Consider the following reaction between cerium(IV) and thallium(I) ions:

    $2Ce^{4+} + Tl^{+} \rightarrow 2Ce^{3+} + Tl^{3+}$

    This reaction is slow, but $Mn^{2+}$ catalyzes it, as shown in the following mechanism:

    $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

    $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

    $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

    In what way does $Mn^{2+}$ increase the reaction rate?
8. The text identifies several factors that limit the industrial applications of enzymes. Still, there is keen interest in understanding how enzymes work for designing catalysts for industrial applications. Why?
9. Most enzymes have an optimal pH range; however, care must be taken when determining pH effects on enzyme activity. A decrease in activity could be due to the effects of changes in pH on groups at the catalytic center or to the effects on groups located elsewhere in the enzyme. Both examples are observed in chymotrypsin, a digestive enzyme that is a protease that hydrolyzes polypeptide chains. Explain how a change in pH could affect the catalytic activity due to (a) effects at the catalytic center and (b) effects elsewhere in the enzyme. (*Hint*: remember that enzymes are composed of functional amino acids.)

## Answers

1. A catalyst lowers the activation energy of a reaction. Some catalysts can also orient the reactants and thereby increase the frequency factor. Catalysts have no effect on the change in potential energy for a reaction.
2. 
3. In adsorption, a reactant binds tightly to a surface. Because intermolecular interactions between the surface and the reactant weaken or break bonds in the reactant, its reactivity is increased, and the activation energy for a reaction is often decreased.
4. 
5. 1. Heterogeneous catalysts are easier to recover.
    2. Collision frequency is greater for homogeneous catalysts.

3. Homogeneous catalysts are often more sensitive to temperature.
4. Homogeneous catalysts are often more expensive.

6.

7. The $Mn^{2+}$ ion donates two electrons to $Ce^{4+}$, one at a time, and then accepts two electrons from $Tl^{+}$. Because Mn can exist in three oxidation states separated by one electron, it is able to couple one-electron and two-electron transfer reactions.

8.

9.

## Numerical Problems

1. At some point during an enzymatic reaction, the concentration of the activated complex, called an enzyme–substrate complex (ES), and other intermediates involved in the reaction is nearly constant. When a single substrate is involved, the reaction can be represented by the following sequence of equations:

$$\begin{gathered} enzyme\ (E) + substrate\ (S) \rightleftharpoons \\ enzyme - substrate\ complex\ (ES) \rightleftharpoons \\ enzyme\ (E) + product\ (P) \end{gathered}$$

   This can also be shown as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightarrow}} ES \underset{k_{-2}}{\overset{k_2}{\leftarrow}} E + P$$

   Using molar concentrations and rate constants, write an expression for the rate of disappearance of the enzyme–substrate complex. Typically, enzyme concentrations are small, and substrate concentrations are high. If you were determining the rate law by varying the substrate concentrations under these conditions, what would be your apparent reaction order?

2. A particular reaction was found to proceed via the following mechanism:

   A + B → C + D

   2C → E

   E + A → 3B + F

   What is the overall reaction? Is this reaction catalytic, and if so, what species is the catalyst? Identify the intermediates.

3. A particular reaction has two accessible pathways (A and B), each of which favors conversion of *X* to a different product (*Y* and *Z*, respectively). Under uncatalyzed conditions pathway A is favored, but in the presence of a catalyst pathway B is favored. Pathway B is reversible, whereas pathway A is not. Which product is favored in the presence of a catalyst? without a catalyst? Draw a diagram illustrating what is occurring with and without the catalyst.

4. The kinetics of an enzyme-catalyzed reaction can be analyzed by plotting the reaction rate versus the substrate concentration. This type of analysis is referred to as a Michaelis–Menten treatment. At low substrate concentrations, the plot shows behavior characteristic of first-order kinetics, but at very high substrate concentrations, the behavior shows zeroth-order kinetics. Explain this phenomenon.

## Answers

1. $\frac{\Delta\left(ES\right)}{\Delta t} = -\left(k_2 + k_{-1}\right)\left[ES\right] + k_1\left[E\right]\left[S\right] + k_{-2}\left[E\right]\left[P\right] \approx 0$; zeroth order in substrate.

2.

3. In both cases, the product of pathway A is favored. All of the *Z* produced in the catalyzed reversible pathway B will eventually be converted to *X* as *X* is converted irreversibly to *Y* by pathway A.

   $Z \underset{B}{\rightleftharpoons} X \overset{A}{\rightarrow} Y$

4.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# CHAPTER OVERVIEW

## 15: Chemical Equilibrium


15.1: The Concept of Chemical Equilibrium
15.2: The Equilibrium Constant
15.3: Solving Equilibrium Problems
15.4: Non-equilibrium Conditions
15.5: Factors That Affect Equilibrium
15.6: Controlling the Products of Reactions
15.7: Essential Skills 7



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# 15.1: The Concept of Chemical Equilibrium

**Learning Objectives**

- To understand what is meant by chemical equilibrium.

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($N_2O_4$) to nitrogen dioxide ($NO_2$). You may recall from Chapter 14 that $NO_2$ is responsible for the brown color we associate with smog. When a sealed tube containing solid $N_2O_4$ (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of $NO_2$ appears (Figure 15.1.1). The reaction can be followed visually because the product ($NO_2$) is colored, whereas the reactant ($N_2O_4$) is colorless:

$$N_2O_4(g) colorless \rightleftharpoons 2NO_{2(g)}\ red-brown \tag{15.1.1}$$

The double arrow indicates that both the forward and reverse reactions are occurring simultaneously; it is read “is in equilibrium with.”



Figure 15.1.1 The **$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ System at Different Temperatures** (left) At dry ice temperature (−78.4°C), the system contains essentially pure solid $N_2O_4$, which is colorless. (center) As the system is warmed above the melting point of $N_2O_4$ (−9.3°C), the $N_2O_4$ melts and then evaporates, and some of the vapor dissociates to red-brown $NO_2$. (right) Eventually the sample reaches room temperature, and a mixture of gaseous $N_2O_4$ and $NO_2$ is present. The composition of the mixture and hence the color do not change further with time: the system has reached equilibrium at the new temperature.

Figure 15.1.2shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of $NO_2$ were zero, then it increases as the concentration of $N_2O_4$ decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no $N_2O_4$ but an initial $NO_2$ concentration twice the initial concentration of $N_2O_4$ in part (a) in Figure 15.1.2, in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition, as shown in part (b) in Figure 15.1.2. Thus equilibrium can be approached from *either direction* in a chemical reaction.

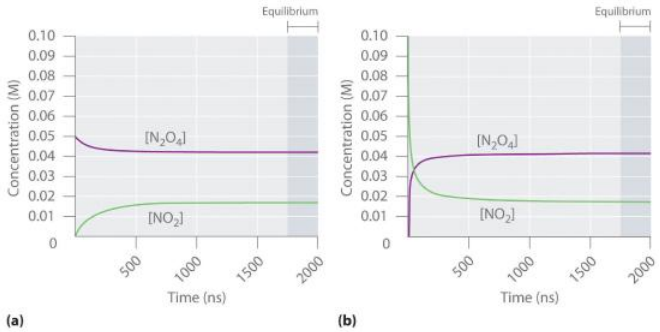



Figure 15.1.2 The Composition of $N_2O_4/NO_2$ Mixtures as a Function of Time at Room Temperature (a) Initially, this idealized system contains 0.0500 M gaseous $N_2O_4$ and no gaseous $NO_2$. The concentration of $N_2O_4$ decreases with time as the concentration of $NO_2$ increases. (b) Initially, this system contains 0.1000 M $NO_2$ and no $N_2O_4$. The concentration of $NO_2$ decreases with time as the concentration of $N_2O_4$ increases. In both cases, the final concentrations of the substances are the same: $[N_2O_4] = 0.0422$ M and $[NO_2] = 0.0156$ M at equilibrium.

Figure 15.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure $NO_2$. Because the initial concentration of $N_2O_4$ is zero, the forward reaction rate (dissociation of $N_2O_4$) is initially zero as well. In contrast, the reverse reaction rate (dimerization of $NO_2$) is initially very high ($2.0 \times 10^6$ M/s), but it decreases rapidly as the concentration of $NO_2$ decreases. (Recall from Chapter 14 that the reaction rate of the dimerization reaction is expected to decrease rapidly because the reaction is second order in $NO_2$: rate = $k_r[NO_2]^2$, where $k_r$ is the rate constant for the reverse reaction shown in Equation 15.1.1.) As the concentration of $N_2O_4$ increases, the rate of dissociation of $N_2O_4$ increases—but more slowly than the dimerization of $NO_2$—because the reaction is only first order in $N_2O_4$ (rate = $k_f[N_2O_4]$, where $k_f$ is the rate constant for the forward reaction in Equation 15.1.1). Eventually, the forward and reverse reaction rates become identical, $k_F = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at *different* rates, then the system is *not* at equilibrium.

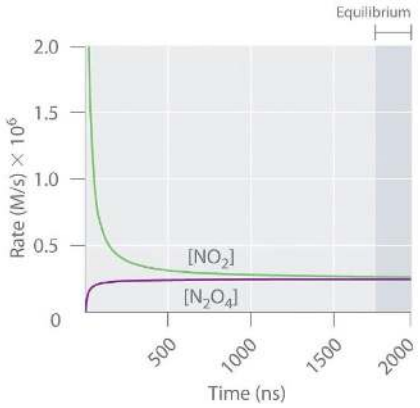



Figure 15.1.2

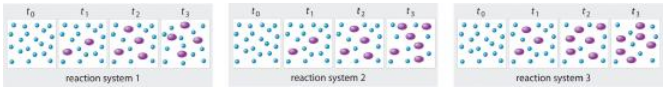
The rate of dimerization of $NO_2$ (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of $N_2O_4$ is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the $N_2O_4$ concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of $N_2O_4$ and $NO_2$ no longer change.

## Note the Pattern

At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

## Example 15.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation <math display="inline" xml:id="av_1.0-15_m004"><semantics><mrow><mn>2</mn><mtext>A</mtext><mo>⇌</mo><mtext>B, </mtext></mrow></semantics></math> where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?




**Given:** three reaction systems

**Asked for:** relative time to reach chemical equilibrium

**Strategy:**

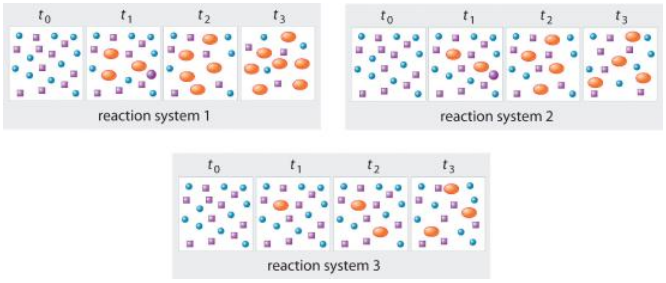
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

**Solution:**

In systems 1 and 3, the concentration of A decreases from $t_0$ through $t_2$ but is the same at both $t_2$ and $t_3$. Thus systems 1 and 3 are at equilibrium by $t_3$. In system 2, the concentrations of A and B are still changing between $t_2$ and $t_3$, so system 2 may not yet have reached equilibrium by $t_3$. Thus system 2 took the longest to reach chemical equilibrium.

Exercise

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?




**Answer:** system 2

## Summary

**Chemical equilibrium** is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

## Key Takeaway

- At equilibrium, the forward and reverse reactions of a system proceed at equal rates.

## Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the concentrations or amounts of the reactants and the products?
2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.
3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of NaCl in water. What is occurring on a microscopic level? What is happening on a macroscopic level?
4. Which of these systems exists in a state of chemical equilibrium?
    1. oxygen and hemoglobin in the human circulatory system
    2. iodine crystals in an open beaker

3. the combustion of wood
4. the amount of $^{14}C$ in a decomposing organism

## Answer

1.
2.
3. Both forward and reverse reactions occur but at the same rate. $Na^+$ and $Cl^-$ ions continuously leave the surface of an NaCl crystal to enter solution, while at the same time $Na^+$ and $Cl^-$ ions in solution precipitate on the surface of the crystal.
4.

- Anonymous

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# 15.2: The Equilibrium Constant

**Learning Objectives**

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the system described in Equation 15.2.1, the decomposition of $N_2O_4$ to $NO_2$. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{15.2.1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{15.2.2}$$

At equilibrium, the forward rate equals the reverse rate:

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{15.2.3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.2.4}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (*K*)The ratio of the rate constants for the forward reaction and the reverse reaction; that is, K =$k_f/k_r$ It is also the equilibrium constant calculated from solution concentrations: K = $[C]^c[D]^d/[A]^a[B]^b$ for the general reaction aA + bB ⇌cC +dD in which each component is in solution. which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{15.2.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: *under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.*

## Note the Pattern

The equilibrium constant is equal to the rate constant for the *forward* reaction divided by the rate constant for the *reverse* reaction.

Table 15.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 15.1.1. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of $NO_2$ and $N_2O_4$ are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will *always* be 6.53 ± 0.03 × $10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

**Table 15.2.1 Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C**

| | Initial Concentrations | | Concentrations at Equilibrium | | |
|---|---|---|---|---|---|
| Experiment | $[N_2O_4]$ (M) | $[NO_2]$ (M) | $[N_2O_4]$ (M) | $[NO_2]$ (M) | $K = [NO_2]^2/[N_2O_4]$ |
| 1 | 0.0500 | 0.0000 | 0.0417 | 0.0165 | $6.54 \times 10^{-3}$ |
| 2 | 0.0000 | 0.1000 | 0.0417 | 0.0165 | $6.54 \times 10^{-3}$ |
| 3 | 0.0750 | 0.0000 | 0.0647 | 0.0206 | $6.56 \times 10^{-3}$ |
| 4 | 0.0000 | 0.0750 | 0.0304 | 0.0141 | $6.54 \times 10^{-3}$ |
| 5 | 0.0250 | 0.0750 | 0.0532 | 0.0186 | $6.50 \times 10^{-3}$ |

## Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for *any* reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{15.2.6}$$

where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass actionFor the general balanced chemical equation aA+bB = cC+ dD the equilibrium constant expression is K =$[C]^c[D]^d/[A]^a[B]^b$ and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.2.7}$$

where *K* is the equilibrium constant for the reaction. Equation 15.7 is called the equilibrium equationFor the general balanced chemical equation aA+bB = cC+ dD the equilibrium constant expression is K =$[C]^c[D]^d/[A]^a[B]^b$, and the right side of Equation 15.2.7 is called the equilibrium constant expression. The relationship shown in Equation 15.2.7 is true for *any* pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of *K* shown in Table 15.2.2 , for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of *K* greater than $10^3$ indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between $H_2$ and $Cl_2$ to produce HCl, which has an equilibrium constant of $1.6 \times 10^{33}$ at 300 K. Because $H_2$ is a good reductant and $Cl_2$ is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of *K* less than $10^{-3}$ indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

**Table 15.2.2 Equilibrium Constants for Selected Reactions***

| Reaction | Temperature (K) | Equilibrium Constant ($K$) |
|---|---|---|
| $S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ | 300 | $4.4 \times 10^{53}$ |
| $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$ | 500 | $2.4 \times 10^{47}$ |
| $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$ | 300 | $1.6 \times 10^{33}$ |
| $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$ | 300 | $4.1 \times 10^{18}$ |
| $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ | 300 | $4.2 \times 10^{13}$ |
| $3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$ | 300 | $2.7 \times 10^{8}$ |
| $H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$ | 100 | 1.92 |
| $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ | 300 | $2.9 \times 10^{-1}$ |
| $I_{2(g)} \rightleftharpoons 2I_{(g)}$ | 800 | $4.6 \times 10^{-7}$ |
| $Br_{2(g)} \rightleftharpoons 2Br_{(g)}$ | 1000 | $4.0 \times 10^{-7}$ |
| $Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$ | 1000 | $1.8 \times 10^{-9}$ |
| $F_{2(g)} \rightleftharpoons 2F_{(g)}$ | 500 | $7.4 \times 10^{-13}$ |

*Equilibrium constants vary with temperature. The $K$ values shown are for systems at the indicated temperatures.

You will also notice in Table 15.2.2 that equilibrium constants have no units, even though Equation 15.2.7 suggests that the units of concentration might not always cancel because the exponents may vary. In fact, equilibrium constants are calculated using "effective concentrations," or *activities*, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M. As shown in Equation 15.2.8, the units of concentration cancel, which makes $K$ unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{15.2.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{15.10}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{15.2.1}$$

with $K$ varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of $H_2$, $D_2$, and HD contains significant concentrations of both product and reactants.

Figure 15.2.1summarizes the relationship between the magnitude of $K$ and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equation 15.2.8 and Equation 15.2.7), when $k_f >> k_r$, $K$ is a large number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f << k_r$, $K$ is a very small number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

Figure 15.2.1 The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium **Constant**The larger the *K*, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

### Note the Pattern

A large value of the equilibrium constant *K* means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

### Example 15.2.1

Write the equilibrium constant expression for each reaction.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2. $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
3. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

**Given:** balanced chemical equations

**Asked for:** equilibrium constant expressions

**Strategy:**

Refer to Equation 15.2.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

**Solution:**

1. The only product is ammonia, which has a coefficient of 2. For the reactants, $N_2$ has a coefficient of 1 and $H_2$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

2. The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $O_2$, with a coefficient of 1/2 Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$

3. This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $O_2$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

Exercise

Write the equilibrium constant expression for each reaction.

1. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
2. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
3. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

**Answer**

1. $K = \dfrac{[N_2][O_2]^{1/2}}{[N_2O]}$
2. $K = \dfrac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
3. $K = \dfrac{[HI]^2}{[H_2][I_2]}$

### Example 15.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

**Given:** systems and values of *K*

**Asked for:** composition of systems at equilibrium

**Strategy:**

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

**Solution:**

1. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
2. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
3. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as $K_{25°C} = 3.3 \times 10^8$, $K_{177°C} = 2.6 \times 10^3$, and $K_{327°C} = 4.1$.

1. At which temperature would you expect to find the highest proportion of $H_2$ and $N_2$ in the equilibrium mixture?
2. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

**Answer**

1. 327°C, where *K* is smallest
2. 25°C

## Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 15.7 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{15.2.10}$$

The corresponding equilibrium constant $K'$ is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{15.2.11}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.2.12}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$ the equilibrium constant $K'$ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{15.2.13}$$

Consider another example, the formation of water: $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ Because $H_2$ is a good reductant and $O_2$ is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form $O_2$ and $H_2$, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into $H_2$ and $O_2$.

### Note the Pattern

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{15.2.2}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{15.2.3}$$

with the equilibrium constant $K''$ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{15.2.14}$$

The values for $K'$ (Equation 15.2.13) and $K''$ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{15.2.15}$$

In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by $n$, then the new equilibrium constant is the original equilibrium constant raised to the $n$th power.

### Example 15.2.3

At 745 K, $K$ is 0.118 for the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is the equilibrium constant for each related reaction at 745 K?

1. $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$
2. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

**Given:** balanced equilibrium equation, $K$ at a given temperature, and equations of related reactions

**Asked for:** values of $K$ for related reactions

**Strategy:**

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate $K$ for each reaction.

**Solution:**

The equilibrium constant expression for the given reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

1. This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

2. In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

Exercise

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

is $7.9 \times 10^4$. Calculate the equilibrium constant for the following reaction at the same temperature:

\[SO_{3(g)} \rightleftharpoons SO_{2(g)}+\frac{1}{2}O_{2(g) \notag \]

**Answer:** $3.6 \times 10^{-3}$

## Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol $K_p$An equilibrium constant expressed as the ratio of the partial pressures of the products and reactants, each raised to its coefficient in the chemical equation. is used to denote equilibrium constants calculated from partial pressures. For the general reaction aA + bB ⇌ cC + dD in which all the components are gases, we can write the equilibrium constant expression as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{15.2.16}$$

Thus $K_p$ for the decomposition of $N_2O_4$ (Equation 15.1.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{15.2.17}$$

Like $K$, $K_p$ is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity.The “effective pressure” is called the *fugacity*, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of $K$ and $K_p$ are usually different. They are, however, related by the ideal gas constant ($R$) and the temperature ($T$):

$$K_p = K(RT)^{\Delta n} \tag{15.2.18}$$

where $K$ is the equilibrium constant expressed in units of concentration and $\Delta n$ is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in kelvins. According to

Equation 15.19, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of $N_2O_4$, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction, $K_p = K(RT)^1 = KRT$.

### Example 15.2.4

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is $K_p$ for this reaction at the same temperature?

**Given:** equilibrium equation, equilibrium constant, and temperature

**Asked for:** $K_p$

**Strategy:**

Use the coefficients in the balanced chemical equation to calculate $\Delta n$. Then use Equation 15.19 to calculate $K$ from $K_p$.

**Solution:**

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know $K$, and $T = 745$ K. Thus, from Equation 15.2.15, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because $K_p$ is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise

Calculate $K_p$ for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

**Answer:** $K_p = 1.2 \times 10^3$

## Homogeneous and Heterogeneous Equilibriums

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibriumAn equilibrium in which the reactants and products of an equilibrium reaction form a single phase, whether gas or liquid.. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibriumAn equilibrium in which the reactants of an equilibrium reaction, the products, or both are in more than one phase., such as the reaction of a gas with a solid or liquid.

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall from Chapter 11, for example, that the density of water, and thus its volume, changes by only a few percentage points between 0°C and 100°C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{15.2.19}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{15.2.20}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26\ \cancel{g}/\cancel{cm^3}}{12.01\ \cancel{g}/mol} \times 1000\ \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{15.2.21}$$

We can rearrange Equation 15.2.17 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{15.2.22}$$

Incorporating the constant value of [C] into the equilibrium equation for the reaction in Equation 15.2.16,

$$K' = \frac{[CO]^2}{[CO_2]} \tag{15.2.23}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{15.2.24}$$

Incorporating all the constant values into $K'$ or $K_p$ allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and $CO_2$, the system described in Equation 15.2.16 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 15.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

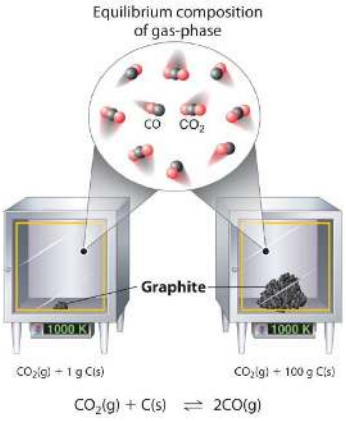



Figure 15.2.2 Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

## Example 15.2.5

Write each expression for $K$, incorporating all constants, and $K_p$ for the following equilibrium reactions.

1. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
2. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

**Given:** balanced equilibrium equations

**Asked for:** expressions for $K$ and $K_p$

**Strategy:**

Find $K$ by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express $K_p$ as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

**Solution:**

1. This reaction contains a pure solid ($PCl_5$) and a pure liquid ($PCl_3$). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]}$$

and

$$K_p = \frac{1}{P_{Cl_2}}$$

2. This reaction contains two pure solids ($Fe_3O_4$ and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4}$$

Exercise

Write the expressions for $K$ and $K_p$ for the following reactions.

1. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
2. $\underset{glucose}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

**Answer**

1. $K = [CO_2]$; and $K_p = P(CO_2)$
2. $K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

### Note the Pattern

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

## Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of $N_2$ with $O_2$ to give $NO_2$. As we stated in Section 15.1, this reaction is an important source of the $NO_2$ that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), $N_2$ reacts with $O_2$ at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional $O_2$ to give $NO_2$ (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$

2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad K_2 = 6.4 \times 10^9$
3. Summing reactions (1) and (2) gives the overall reaction of $N_2$ with $O_2$:
4. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

v

What is the relationship between $K_1$, $K_2$, and $K_3$, all at 100°C? The expression for $K_1$ has $[NO]^2$ in the numerator, the expression for $K_2$ has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for $K_3$. Multiplying $K_1$ by $K_2$ and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for $K_1$ and $K_2$ is the same as the equilibrium constant expression for $K_3$:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^9) = 1.3 \times 10^{-15}$$

*The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions.* In contrast, recall that according to Hess's Law, $\Delta H$ for the sum of two or more reactions is the *sum* of the $\Delta H$ values for the individual reactions.

### Note the Pattern

To determine $K$ for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

### Example 15.2.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \quad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \quad K_2 = 3.3 \times 10^4$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \quad K_3 = ?$

**Given:** two balanced equilibrium equations, values of $K$, and an equilibrium equation for the overall reaction

**Asked for:** equilibrium constant for the overall reaction

**Strategy:**

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of $K$ for that equation. Calculate $K$ for the overall equation by multiplying the equilibrium constants for the individual equations.

**Solution:**

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for $K_1$ and $K_2$ are given, so it is straightforward to calculate $K_3$:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3$$

Exercise

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \quad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \quad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \quad K_3 = ?$

**Answer:** $K_3 = 1.1 \times 10^{66}$

## Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the **equilibrium constant (*K*)**, a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same *K*. For a system at equilibrium, the **law of mass action** relates *K* to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the **equilibrium equation**. The ratio is called the **equilibrium constant expression**. When a reaction is written in the reverse direction, *K* and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures ($K_\mathbf{p}$) is related to *K* by the ideal gas constant (*R*), the temperature (*T*), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a **homogeneous equilibrium**; a system whose reactants, products, or both are in more than one phase is a **heterogeneous equilibrium**. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

## Key Takeaways

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.

## Key Equations

**Definition of equilibrium constant in terms of forward and reverse rate constants**

Equation 15.2.5: $K = \frac{k_f}{k_r}$

**Equilibrium constant expression (law of mass action)**

Equation 15.2.7: $<K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

**Equilibrium constant expression for reactions involving gases using partial pressures**

Equation 15.2.1617: $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$

**Relationship between $K_\mathbf{p}$ and $K$**

Equation 15.2.18: $K_p = K\,(RT)^{\Delta n}$

## Conceptual Problems

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?
2. Which of the following equilibriums are homogeneous and which are heterogeneous?
    1. $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$

2. $C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$
3. $H_2C{=}CH_{2(g)} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}$
4. $2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$

3. Classify each equilibrium system as either homogeneous or heterogeneous.

1. $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
2. $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
3. $2Mg_{(s)} + O_{2(g)} \rightleftharpoons 2MgO_{(s)}$
4. $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

4. If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?

5. Industrial production of NO by the reaction <math xml:id="av_1.0-15_m114" display="inline"><semantics><mrow><msub><mtext>N</mtext><mn>2</mn></msub><mtext>(g)</mtext><mo>+</mo><msub><mtext>O</mtext><mn>2</mn></msub><mtext>(g)</mtext><mo>⇌</mo><mtext>2NO(g)</mtext></mrow></semantics></math> is carried out at elevated temperatures to drive the reaction toward the formation of product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?

6. How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?

7. What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?

8. Write the equilibrium constant expressions for $K$ and $K_p$ for each reaction.

1. $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$
2. $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
3. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

9. Write the equilibrium constant expressions for $K$ and $K_p$ as appropriate for each reaction.

1. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
2. $\frac{1}{2}H_{2(g)} + 12I_{2(g)} \rightleftharpoons HI_{(g)}$
3. $cis-stilbene_{(soln)} \rightleftharpoons trans-stilbene_{(soln)}$

10. Why is it incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression?

11. Write the equilibrium constant expressions for $K$ and $K_p$ for each equilibrium reaction.

1. $2S_{(s)} + 3O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
2. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$
3. $2ZnS_{(s)} + 3O_{2(g)} \rightleftharpoons 2ZnO_{(s)} + 2SO_{2(g)}$

12. Write the equilibrium constant expressions for $K$ and $K_p$ for each equilibrium reaction.

1. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + O_{2(g)}$
2. $H_{2(g)} + I_{2(s)} \rightleftharpoons 2HI_{(g)}$
3. $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$

13. At room temperature, the equilibrium constant for the reaction <math xml:id="av_1.0-15_m134" display="inline"><semantics><mrow><mn>2</mn><mtext>A(g)</mtext><mo>⇌</mo><mtext>B(g)</mtext></mrow></semantics></math> is 1. What does this indicate about the concentrations of A and B at equilibrium? Would you expect $K$ and $K_p$ to vary significantly from each other? If so, how would their difference be affected by temperature?

14. For a certain series of reactions, if $[OH^-][HCO_3^-]/[CO_3^{2-}] = K_1$ and $[OH^-][H_2CO_3]/[HCO_3^-] = K_2$, what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.

15. In the equation for an enzymatic reaction, ES represents the complex formed between the substrate S and the enzyme protein E. In the final step of the following oxidation reaction, the product P dissociates from the $ESO_2$ complex, which regenerates the active enzyme:

$$E + S \rightleftharpoons ES \qquad K_1 \tag{15.2.4}$$

$$ES + O_2 \rightleftharpoons ESO_2 \qquad K_2 \tag{15.2.5}$$

$$ESO_2 \rightleftharpoons E + P \qquad K_3 \tag{15.2.6}$$

Give the overall reaction equation and show that $K = K_1 \times K_2 \times K_3$.

## Answers

1. The equilibrium constant for the reaction written in reverse: $K' = 1/K$.
2. 
3. Each system is heterogeneous.
4. 
5. Rapid cooling “quenches” the reaction mixture and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.
6. 
7. \(K=\dfrac{k_f}{k_r\;\;\; K=\dfrac{[C]^c[D]^d}{[A]^a[B]^b}\]
8. 
9. 1. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]} \quad K_p = \dfrac{(P_{N_2O})^2}{(P_{NO})^2(P_{O_2}}$)
   2. $K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} \quad K_p = \dfrac{P_{HI}}{(P_{H_2})^{1/2}(P_{I_2})}$
   3. $K = \dfrac{[\text{trans-stilbene}]}{[\text{cis-stilbene}]}$
10. 
11. 1. $K = \dfrac{[SO_3]^2}{[O_2]^3} \quad K_p = \dfrac{(P_{SO_3})^2}{(P_{O_2})^3}$
    2. $K = \dfrac{[CO]^2}{[CO_2]} \quad K_p = \dfrac{(P_{CO})^2}{P_{CO_2}}$
    3. $K = \dfrac{[SO_2]^2}{[O_2]^3} \quad K_p = \dfrac{(P_{SO_2})^2}{(P_{O_2})^3}$
12. 
13. At equilibrium,

$$[A] = \sqrt{B} \text{ and } \Delta n = -1 \text{ so } K_p = K(RT)^{\Delta n} = \frac{K}{RT}$$

the difference increases as $T$ increases.

14. 
15. 

## Numerical Problems

1. Explain what each of the following values for $K$ tells you about the relative concentrations of the reactants versus the products in a given equilibrium reaction: $K = 0.892$; $K = 3.25 \times 10^8$; $K = 5.26 \times 10^{-11}$. Are products or reactants favored at equilibrium?
2. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.
   1. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
   2. $\frac{1}{2}N_2O_{4(g)} \rightleftharpoons NO_{2(g)}$
3. Write the equilibrium constant expression for each reaction.

1. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$
2. $\frac{1}{3}N_{2(g)} + H_{2(g)} \rightleftharpoons \frac{2}{3}NH_{3(g)}$

How are these two expressions mathematically related to the equilibrium constant expression for

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}?$$

4. Write an equilibrium constant expression for each reaction.
   1. $C_{(s)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 2H_{2(g)}$
   2. $SbCl_{3(g)} + Cl_{2(g)} \rightleftharpoons SbCl_{5(g)}$
   3. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$
5. Give an equilibrium constant expression for each reaction.
   1. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
   2. $\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$
   3. $CaCO_{3(s)} + 2HOCl_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OCl^{-}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
6. Calculate $K$ and $K_p$ for each reaction.
   1. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{(g)}$ at 727°C, the equilibrium concentration of NO is 1.29 M, $Br_2$ is 10.52 M, and NOBr is 0.423 M.
   2. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$: at 1200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm $CO_2$ and 76.8 atm CO, and the vessel contains 3.55 g of carbon.
7. Calculate $K$ and $K_p$ for each reaction.
   1. $N_2O4_{(g)} \rightleftharpoons 2NO_{2(g)}$: at the equilibrium temperature of −40°C, a 0.150 M sample of $N_2O_4$ undergoes a decomposition of 0.456%.
   2. $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$: an equilibrium is reached at 227°C in a 15.5 L reaction vessel with a total pressure of 6.71 × $10^2$ atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7193 g of methanol.
8. Determine $K$ and $K_p$ (where applicable) for each reaction.
   1. $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$: at 1065°C, an equilibrium mixture consists of $1.00 \times 10^{-3}$ M $H_2$, $1.20 \times 10^{-3}$ M $S_2$, and $3.32 \times 10^{-3}$ M $H_2S$.
   2. $Ba(OH)_{2(s)} \rightleftharpoons 2OH^{-}_{(aq)} + Ba^{2+}_{(aq)}$: at 25°C, a 250 mL beaker contains 0.330 mol of barium hydroxide in equilibrium with 0.0267 mol of barium ions and 0.0534 mol of hydroxide ions.
9. Determine $K$ and $K_p$ for each reaction.
   1. $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$: at 500 K, a 24.3 mM sample of $NOCl$ has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of $NOCl$.
   2. $Cl_{2(g)} + PCl_{3(g)} \rightleftharpoons PCl_{5(g)}$: at 250°C, a 500 mL reaction vessel contains 16.9 g of $Cl_2$ gas, 0.500 g of $PCl_3$, and 10.2 g of $PCl_5$ at equilibrium.
10. The equilibrium constant expression for a reaction is $[CO_2]^2/[SO_2]^2[O_2]$. What is the balanced chemical equation for the overall reaction if one of the reactants is $Na_2CO_3$(s)?
11. The equilibrium constant expression for a reaction is $[NO][H_2O]^{3/2}/[NH_3][O_2]^{5/4}$. What is the balanced chemical equation for the overall reaction?
12. Given $K = k_f/k_r$, what happens to the magnitude of the equilibrium constant if the reaction rate of the forward reaction is doubled? What happens if the reaction rate of the reverse reaction for the overall reaction is decreased by a factor of 3?
13. The value of the equilibrium constant for

$$2H_{2(g)} + S_{2(g)} \rightleftharpoons 2H_2S_{(g)}$$

is 1.08 × $10^7$ at 700°C. What is the value of the equilibrium constant for the following related reactions?

   1. $H_{2(g)} + 12S_{2(g)} \rightleftharpoons H_2S_{(g)}$
   2. $4H_{2(g)} + 2S_{2(g)} \rightleftharpoons 4H_2S_{(g)}$

3. $H_2S_{(g)} \rightleftharpoons H_{2(g)} + 12S_{2(g)}$

## Answers

1. $K$ = 0.892: the concentrations of the products and the reactants are approximately equal at equilibrium so neither is favored; $K$ = 3.25 × $10^8$: the ratio of the concentration of the products to the reactants at equilibrium is very large so the formation of products is favored; $K = 5.26 \times 10^{-11}$: the ratio of the concentration of the products to the reactants at equilibrium is very small so the formation of products is not favored.
2. 
3. 1. $K' = \dfrac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$
   2. $K'' = \dfrac{[NH_3]^{2/3}}{[N_2]^{1/3}[H_2]} \quad K = \dfrac{[NH_3]^2}{[N_2][H_2]^3} \quad K' = K^{1/2}, \text{ and} K'' = K^{1/3}$
4. 
5. 1. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$
   2. $K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$
   3. $K = \dfrac{[Ca^{2+}][OCl^-]^2[P_{CO_2}]}{[HOCl]^2}$
6. 
7. 1. $K = 1.25 \times 10^{-5} \quad K_p = 2.39 \times 10^{-4}$
   2. $K = 9.43 \quad K_p = 5.60 \times 10^{-3}$
8. 
9. 1. $K = \dfrac{[Cl_2][NO]^2}{[NOCl]^2} = 4.59 \times 10^{-4} \quad K_p = 1.88 \times 10^{-2}$
   2. $K = \dfrac{[PCl_5]}{[PCl_3][Cl_2]} = 28.3 \quad K_p = 0.658$
10. 
11. $NH_3 + \frac{5}{4}O_2 \rightleftharpoons NO + \frac{3}{2}H_2O$, which can also be written as follows:

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)} \tag{15.2.7}$$

12. 
13. 1. 3.29 × $10^3$
    2. 1.17 × $10^{14}$
    3. 3.04 × $10^{-4}$

- Anonymous

Modified by Joshua B. Halpern

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# 15.3: Solving Equilibrium Problems

**Learning Objectives**

- To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems: (1) those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and (2) those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

## Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_3$(s) to CaO(s) and $CO_2$(g) is $K = [CO_2]$. At 800°C, the concentration of $CO_2$ in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}$ M. Thus $K$ at 800°C is $2.5 \times 10^{-3}$. (Remember that equilibrium constants are unitless.)



A more complex example of this type of problem is the conversion of *n*-butane, an additive used to increase the volatility of gasoline, to isobutane (2-methylpropane). This reaction can be written as follows:

$$n-butane\,(g) \rightleftharpoons isobutane\,(g)$$

and the equilibrium constant $K$ = [isobutane]/[*n*-butane]. At equilibrium, a mixture of *n*-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M *n*-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{isobutane}{n-butane} = \frac{0.041\ \cancel{M}}{0.016\ \cancel{M}} = 2.6$$

Thus the equilibrium constant for the reaction as written is 2.6.

### Example 15.3.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

A mixture of $SO_2$ and $O_2$ was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained $5.0 \times 10^{-2}$ M $SO_3$, $3.5 \times 10^{-3}$ M $O_2$, and $3.0 \times 10^{-3}$ M $SO_2$. Calculate $K$ and $K_p$ at this temperature.

**Given:** balanced equilibrium equation and composition of equilibrium mixture

**Asked for:** equilibrium constant

**Strategy:**

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain $K$.

**Solution:**

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(5.0 \times 10^{-2}\right)^2}{\left(3.0 \times 10^{-3}\right)^2\left(3.5 \times 10^{-3}\right)} = 7.9 \times 10^4$$

To solve for $K_p$, we use Equation 15.2.17, where $\Delta n = 2 - 3 = -1$:

$$\begin{aligned} K_p &= K(RT)^{\Delta n} \\ &= 7.9 \times 10^4 \left[\left(0.082606\ L \cdot atm/mol \cdot \cancel{K}\right)\left(800\ \cancel{K}\right)\right] \\ &= 1.2 \times 10^3 \end{aligned}$$

Exercise

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

A mixture of $H_2$ and $I_2$ was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained $1.37 \times 10^{-2}$ M HI, $6.47 \times 10^{-3}$ M $H_2$, and $5.94 \times 10^{-4}$ M $I_2$. Calculate $K$ and $K_p$ for this reaction.

**Answer:** $K = 48.8$; $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 9 shows one way to do this.

### Example 15.3.2

A 1.00 mol sample of NOCl was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of $Cl_2$. Calculate $K$ at this temperature. The equation for the decomposition of NOCl to NO and $Cl_2$ is as follows:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

**Given:** balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

**Asked for:** $K$

**Strategy:**

**A** Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

**B** Calculate all possible initial concentrations from the data given and insert them in the table.

**C** Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

**D** Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

**Solution:**

**A** The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO_2]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of NOCl, NO, and $Cl_2$ at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

| $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$ | | | |
|---|---|---|---|
| | [NOCl] | [NO] | $[Cl_2]$ |
| initial | | | |
| change | | | |
| final | | | |

**B** Initially, the system contains 1.00 mol of NOCl in a 2.00 L container. Thus $[NOCl]_i$ = 1.00 mol/2.00 L = 0.500 M. The initial concentrations of NO and $Cl_2$ are 0 M because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of $Cl_2$ in a 2.00 L container, so $[Cl_2]_f$ = 0.056 mol/2.00 L = 0.028 M. We insert these values into the following table:

| $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$ | | | |
|---|---|---|---|
| | [NOCl] | [NO] | $[Cl_2]$ |
| initial | 0.500 | 0 | 0 |
| change | | | |
| final | | | 0.028 |

**C** We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of $Cl_2$, the substance for which initial and final concentrations are known:

$\Delta[Cl_2]$ = [0.028 M (final) − 0.00 M (initial)] = +0.028 M

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of $Cl_2$, so the change in the NO concentration is as follows:

$$\Delta\,[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of NOCl are consumed for every 1 mol of $Cl_2$ produced, so the change in the NOCl concentration is as follows:

$$\Delta\,[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

| $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$ | | | |
|---|---|---|---|
| | [NOCl] | [NO] | $[Cl_2]$ |
| initial | 0.500 | 0 | 0 |
| change | −0.056 | +0.056 | +0.028 |
| final | | | 0.028 |

**D** We sum the numbers in the [NOCl] and [NO] columns to obtain the final concentrations of NO and NOCl:

$[NO]_f$ = 0.000 M + 0.056 M = 0.056 M $[NOCl]_f$ = 0.500 M + (−0.056 M) = 0.444 M

We can now complete the table:

| $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$ | | | |
|---|---|---|---|
| | [NOCl] | [NO] | $[Cl_2]$ |
| initial | 0.500 | 0 | 0 |
| change | −0.056 | +0.056 | +0.028 |
| final | 0.444 | 0.056 | 0.028 |

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO_2]^2\,[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2\,(0.028)^2}{0.444} = 4.5 \times 10^{-4}$$

Exercise

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia ($NH_3$) by reacting 0.1248 M $H_2$ and 0.0416 M $N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M $NH_3$. What is $K$ for the reaction $N_2 + 3\ H_2 \rightleftharpoons 2NH_3$at this temperature? What is $K_p$?

**Answer:** $K = 0.105$; $K_p = 2.61 \times 10^{-5}$



**The original laboratory apparatus designed by Fritz Haber and Robert Le Rossignol in 1908 for synthesizing ammonia from its elements.** A metal catalyst bed, where ammonia was produced, is in the large cylinder at the left. The Haber-Bosch process used for the industrial production of ammonia uses essentially the same process and components but on a much larger scale. Unfortunately, Haber's process enabled Germany to prolong World War I when German supplies of nitrogen compounds, which were used for explosives, had been exhausted in 1914.

## Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of *n*-butane to isobutane (Equation 15.26), for which $K = 2.6$ at 25°C. If we begin with a 1.00 M sample of *n*-butane, we can determine the concentration of *n*-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 9.

| nbutane(g) ⇌isobutane(g) | | |
|---|---|---|
| | [*n*-Butane] | [Isobutane] |
| initial | | |
| change | | |
| final | | |

The initial concentrations of the reactant and product are both known: $[n\text{-butane}]_i = 1.00$ M and $[\text{isobutane}]_i = 0$ M. We need to calculate the equilibrium concentrations of both *n*-butane and isobutane. Because it is generally difficult to calculate final

concentrations directly, we focus on the *change* in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as +*x*, then the change in the concentration of *n*-butane is Δ[*n*-butane] = −*x*. This is because the balanced chemical equation for the reaction tells us that 1 mol of *n*-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

| nbutane(g) ⇌isobutane(g) | | |
|---|---|---|
| | [*n*-Butane] | [Isobutane] |
| initial | 1.00 | 0 |
| change | −*x* | +*x* |
| final | (1.00 − *x*) | (0 + *x*) = *x* |

Substituting the expressions for the final concentrations of *n*-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[isobutane]}{[n-butane]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for *x*,

$$x = 2.6\,(1.00 - x) = 2.6 - 2.6x$$
$$x + 2.6x = 2.6$$
$$x = 0.72$$

We obtain the final concentrations by substituting this *x* value into the expressions for the final concentrations of *n*-butane and isobutane listed in the table:

[*n*-butane]$_f$ = (1.00 − *x*) M = (1.00 − 0.72) M = 0.28 M [isobutane]$_f$ = (0.00 + *x*) M = (0.00 + 0.72) M = 0.72 M

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same *K* that we used in the calculation:

$$K = \frac{[isobutane]}{[n-butane]} = \frac{0.72\ \cancel{M}}{0.28\ \cancel{M}} = 2.6$$

This is the same *K* we were given, so we can be confident of our results.

Example 10 illustrates a common type of equilibrium problem that you are likely to encounter.

### Example 15.3.3

The *water–gas shift reaction* is important in several chemical processes, such as the production of $H_2$ for fuel cells. This reaction can be written as follows:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)$$

*K* = 0.106 at 700 K. If a mixture of gases that initially contains 0.0150 M $H_2$ and 0.0150 M $CO_2$ is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

**Given:** balanced equilibrium equation, *K*, and initial concentrations

**Asked for:** final concentrations

**Strategy:**

**A** Construct a table showing what is known and what needs to be calculated. Define *x* as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of *x*. From the values in the table, calculate the final concentrations.

**B** Write the equilibrium equation for the reaction. Substitute appropriate values from the table to obtain *x*.

**C** Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain *K*.

**Solution:**

**A** The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150$ M. Just as before, we will focus on the *change* in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of $H_2O$ as *x*, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of *x*. For example, 1 mol of CO is produced for every 1 mol of $H_2O$, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of $H_2O$ produced, 1 mol each of $H_2$ and $CO_2$ are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

| $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ | | | | |
|---|---|---|---|---|
| | $[H_2]$ | $[CO_2]$ | $[H_2O]$ | [CO] |
| initial | 0.0150 | 0.0150 | 0 | 0 |
| change | $-x$ | $-x$ | $+x$ | $+x$ |
| final | $(0.0150 - x)$ | $(0.0150 - x)$ | $x$ | $x$ |

**B** We can now use the equilibrium equation and the given *K* to solve for *x*:

$$K = \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]} = \frac{(x)\,(x)}{(0.0150 - x)\,(0.0150 - x)} = \frac{x^2}{(0.0150 - x)^2} = 0.160$$

We could solve this equation with the quadratic formula, but it is far easier to solve for *x* by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

(The quadratic formula is presented in Essential Skills 7 in Section 15.7 .) Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150 - x)^2} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

**C** The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this *K* is the same as the value given in the problem, so our answer is confirmed.

Exercise

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K$ = 54 at 425°C. If 0.172 M $H_2$ and $I_2$ are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

**Answer:** $[HI]_f = 0.270$ M; $[H_2]_f = [I_2]_f = 0.037$ M

In Example 10, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 11.

### Example 15.3.4

In the water–gas shift reaction shown in Example 10, a sample containing 0.632 M $CO_2$ and 0.570 M $H_2$ is allowed to equilibrate at 700 K. At this temperature, $K$ = 0.106. What is the composition of the reaction mixture at equilibrium?

**Given:** balanced equilibrium equation, concentrations of reactants, and $K$

**Asked for:** composition of reaction mixture at equilibrium

**Strategy:**

**A** Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations ($x$) and the final concentrations.

**B** Write the equilibrium constant expression for the reaction. Substitute the known $K$ value and the final concentrations to solve for $x$.

**C** Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain $K$.

**Solution:**

**A** $[CO_2]_i = 0.632$ M and $[H_2]_i = 0.570$ M. Again, $x$ is defined as the change in the concentration of $H_2O$: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of $H_2O$, the change in the concentration of CO is the same as the change in the concentration of $H_2O$, so $\Delta[CO] = +x$. Similarly, because 1 mol each of $H_2$ and $CO_2$ are consumed for every 1 mol of $H_2O$ produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \tag{15.3.1}$$

| | $[H_2]$ | $[CO_2]$ | $[H_2O]$ | $[CO]$ |
|---|---|---|---|---|
| initial | 0.570 | 0.632 | 0 | 0 |
| change | $-x$ | $-x$ | $+x$ | $+x$ |
| final | $(0.570 - x)$ | $(0.632 - x)$ | $x$ | $x$ |

**B** We can now use the equilibrium equation and the known $K$ value to solve for $x$:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 10, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148$ M, and $\Delta[H_2] = \Delta[CO_2] = -0.148$ M.

**C** The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f [= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because $K$ is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise

The exercise in Example 8 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K$ = 54 at 425°C. If a sample containing 0.200 M $H_2$ and 0.0450 M $I_2$ is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

**Answer:** $[HI]_f$ = 0.0882 M; $[H_2]_f$ = 0.156 M; $[I_2]_f = 9.2 \times 10^{-4}$ M

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \le 10^{-3}$) or very large ($K \ge 10^3$), which means that the change in the concentration (defined as $x$) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 12.

### Example 15.3.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

$K_p = 2.0 \times 10^{-31}$ at 25°C. What is the partial pressure of NO in equilibrium with $N_2$ and $O_2$ in the atmosphere (at 1 atm, $P\{N_2\}$ = 0.78 atm and $P\{O_2\}$ = 0.21 atm

**Given:** balanced equilibrium equation and values of $K_p$, $P\{O_2\}$ and $P\{N_2\}$

**Asked for:** partial pressure of NO

**Strategy:**

**A** Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.

**B** Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration ($x$).

**C** Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for $K$.

**Solution:**

**A** Because we are given $K_p$ and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of $O_2$ is 0.21 atm and that of $N_2$ is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in

the partial pressure of $O_2$ and of $N_2$ is $-x$ because 1 mol each of $N_2$ and of $O_2$ is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \tag{15.3.2}$$

| | P{$N_2$} | P{$N_2$} | P{NO} |
|---|---|---|---|
| initial *P* | 0.78 | 0.21 | 0 |
| change in *P* | $-x$ | $-x$ | $+2x$ |
| final *P* | $(0.78 - x)$ | $(0.21 - x)$ | $2x$ |

**B** Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the *x* value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) = 0.78$ and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^{=} 9.1 \times 10^{-17}$$

**C** Substituting this value of *x* into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding *x* was correct: given two significant figures, $2.0 \times 10^{-16}$ is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if *x* is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of $N_2$ and $O_2$ to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 times 10^{-31}$$

The final $K_p$ agrees with the value given at the beginning of this example.

Exercise

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

$K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere $P(O_2) = 0.21$ atm?

**Answer:** $4.8 \times 10^{-31}$ atm

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the *products* side of the reaction rather than the reactants side. This approach is illustrated in Example 13.

### Example 15.3.6

The chemical equation for the reaction of hydrogen with ethylene ($C_2H_4$) to give ethane ($C_2H_6$) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

$K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M $H_2$ and 0.155 M $C_2H_4$ is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

**Given:** balanced chemical equation, *K*, and initial concentrations of reactants

**Asked for:** equilibrium concentrations

**Strategy:**

**A** Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.

**B** Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for *x* (the change in concentration).

**C** Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

**Solution:**

**A** From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 12. If we define −*x* as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is +*x*. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)} \tag{15.3.3}$$

| | $[H_2]$ | $[C_2H_4]$ | $[C_2H_6]$ |
|---|---|---|---|
| initial | 0.200 | 0.155 | 0 |
| assuming 100% reaction | 0.045 | 0 | 0.155 |
| change | +*x* | +*x* | −*x* |
| final | (0.045 + *x*) | (0 + *x*) | (0.155 − *x*) |

**B** Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus *x* is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be

simplified [(0.045 + $x$) = 0.045 and (0.155 − $x$) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

**C** The small $x$ value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This $K$ value agrees with our initial value at the beginning of the example.

Exercise

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

$K_p$ = 4.0 × $10^{31}$ at 47°C. If a mixture of 0.257 M $H_2$ and 0.392 M $Cl_2$ is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

**Answer:**

- $[H_2]_f = 4.8 \times 10^{-32}\ M$
- $[Cl_2]_f = 0.135\ M$
- $[HCl]_f = 0.514\ M$

## Summary

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

## Key Takeaway

- Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

## Conceptual Problems

1. Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.
2. Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making certain assumptions about the concentrations of products and reactants. What are these assumptions when $K$ is (a) very large and (b) very small? Illustrate this technique using the system A + 2B ⇌ C for which you are to calculate the concentration of the product at equilibrium starting with only A and B. Under what circumstances should simplifying assumptions not be used?

## Numerical Problems

*Please be sure you are familiar with the topics discussed in Essential Skills 7 (Section 15.7 ) before proceeding to the Numerical Problems.*

1. In the equilibrium reaction A + B ⇌C, what happens to $K$ if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction A ⇌B + C?
2. The following table shows the reported values of the equilibrium P{$O_2$} at three temperatures for the reaction $Ag_2O(s)$ ⇌ 2 Ag(s) + 1/2 $O_2(g)$ for which $\Delta H°$ = 31 kJ/mol. Are these data consistent with what you would expect to occur? Why or why not?

| $T$ (°C) | P($O_2$) mm Hg |
|---|---|
| 150 | 182 |
| 184 | 143 |
| 191 | 126 |

3. Given the equilibrium system $N_2O_4(g)$ ⇌ 2 $NO_2(g)$, what happens to $K_p$ if the initial pressure of $N_2O_4$ is doubled? If $K_p$ is 1.7 × $10^{-1}$ at 2300°C, and the system initially contains 100% $N_2O_4$ at a pressure of 2.6 × $10^2$ atm, what is the equilibrium pressure of each component?
4. At 430°C, 4.20 mol of HI in a 9.60 L reaction vessel reaches equilibrium according to the following equation: $H_2(g)$ + $I_2(g)$ ⇌2HI(g) At equilibrium, [$H_2$] = 0.047 M and [HI] = 0.345 M. What are $K$ and $K_p$ for this reaction?
5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction: CO(g) + 2$H_2(g)$ ⇌ $CH_3OH(g)$ and $K_p$ = 1.3 × $10^{-4}$. If 56.0 g of CO is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 atm, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?
6. Starting with pure A, if the total equilibrium pressure is 0.969 atm for the reactionA(s ⇌ 2 B(g) + C(g), what is $K_p$?
7. The decomposition of ammonium carbamate to $NH_3$ and $CO_2$ at 40°C is written as $NH_4CO_2NH_2(s)$ ⇌ 2$NH_3(g)$ + $CO_2$ If the partial pressure of $NH_3$ at equilibrium is 0.242 atm, what is the equilibrium partial pressure of $CO_2$? What is the total gas pressure of the system? What is $K_p$?
8. At 375 K, $K_p$ for the reaction $SO_2Cl_2(g)$ ⇌ $SO_2(g)$ + $Cl_2g$) is 2.4, with pressures expressed in atmospheres. At 303 K, $K_p$ is 2.9 × $10^{-2}$.
    1. What is $K$ for the reaction at each temperature?
    2. If a sample at 375 K has 0.100 M $Cl_2$ and 0.200 M $SO_2$ at equilibrium, what is the concentration of $SO_2Cl_2$?
    3. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb?
9. For the gas-phase reaction aA ⇌ bB, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.
10. For the gas-phase reaction $I_2$ ⇌2I, show that the total pressure is related to the equilibrium pressure by the following equation:

$$P_T = \sqrt{K_p P_{I_2}} + P_{I_2}$$

11. Experimental data on the system Br2(l) ⇌ $Br_2$(aq) are given in the following table. Graph [$Br_2$] versus moles of $Br_2$(l) present; then write the equilibrium constant expression and determine $K$.

| Grams $Br_2$ in 100 mL Water | [$Br_2$] (M) |
|---|---|
| 1.0 | 0.0626 |
| 2.5 | 0.156 |
| 3.0 | 0.188 |
| 4.0 | 0.219 |
| 4.5 | 0.219 |

12. Data accumulated for the reaction n-butane(g) ⇌ isobutane(g) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of *n*-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of *n*-butane and isobutane?

| Moles *n*-butane | Moles Isobutane |
|---|---|
| 0.5 | 1.25 |
| 1.0 | 2.5 |
| 1.50 | 3.75 |

13. Solid ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes:

$$NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$$

At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas? What is $K_p$? If the concentration of $CO_2$ is doubled and then equilibrates to its initial equilibrium partial pressure +*x* atm, what change in the $NH_3$ concentration is necessary for the system to restore equilibrium?

14. The equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is $K_p = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $COCl_2$ is $3.05 \times 10^{-3}$ M, what is the partial pressure of each gas at equilibrium at 100°C? What assumption can be made to simplify your calculations?

15. Aqueous dilution of $IO_4^-$ results in the following reaction:

$$IO^-_{4(aq)} + 2H_2O_{(l)} \rightleftharpoons H_4IO^-_{6(aq)}$$

and $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution of $IO_4^-$ that is diluted to 250 mL with water, how many moles of $H_4IO_6^-$ are formed at equilibrium?

16. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation:

$$I_{2(g)} + Br_{2(g)} \rightleftharpoons 2IBr_{(g)}$$

$K_p = 1.2 \times 10^2$. If you begin the reaction with 7.4 g of $I_2$ vapor and 6.3 g of $Br_2$ vapor in a 1.00 L container, what is the concentration of IBr(g) at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?

17. For the reaction

$$C_{(s)} + 12N_{2(g)} + \frac{5}{2}H_{2(g)} \rightleftharpoons CH3NH2(g)$$

$K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0 mol of $N_2$, 2.0 mol of $H_2$, and sufficient C(s) in a 2.00 L container, what are the concentrations of $N_2$ and $CH_3NH_2$ at equilibrium? What happens to *K* if the concentration of $H_2$ is doubled?

## Contributors

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# 15.4: Non-equilibrium Conditions

**Learning Objectives**

- To predict in which direction a reaction will proceed.

In Section 15.3, we saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

## The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the reaction quotient ($Q$)A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products, regardless of whether the system is at equilibrium: $Q = [C]^c[D]^d/[A]^a[B]^b$ for the general balanced chemical equation $aA + bB \rightleftharpoons cC + dD$. The expression for the reaction quotient has precisely the same form as the equilibrium constant expression, except that $Q$ may be derived from a set of values measured at *any* time during the reaction of *any* mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.4.1}$$

The reaction quotient $Q_p$ analogous to $K_p$, can be written for any reaction that involves gases by using the partial pressures of the components.

To understand how information is obtained using a reaction quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write $Q$ for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.4.2}$$

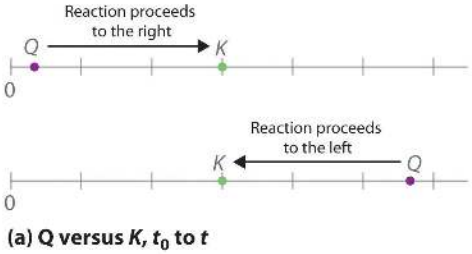
The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of $Q$ were calculated for each. Each experiment begins with different proportions of product and reactant:

| Experiment | $[NO_2]$ (M) | $[N_2O_4]$ (M) | $Q = [NO_2]^2/[N_2O_4]$ |
|---|---|---|---|
| 1 | 0 | 0.0400 | $\frac{0^2}{0.0400} = 0$ |
| 2 | 0.0600 | 0 | $\frac{(0.0600)^2}{0} = \text{undefined}$ |
| 3 | 0.0200 | 0.0600 | $\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$ |

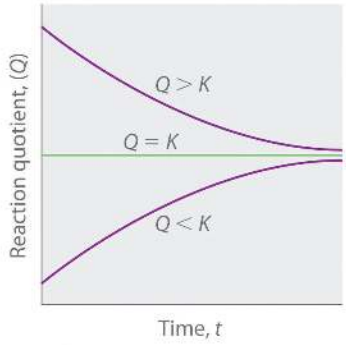
As these calculations demonstrate, $Q$ can have any numerical value between 0 and infinity (undefined); that is, $Q$ can be greater than, less than, or equal to $K$.

Comparing the magnitudes of $Q$ and $K$ enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes $Q$

approach $K$. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is *less* than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is *greater* than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 15.4.1




**(a) Q versus $K$, $t_0$ to $t$**




**(b) Q versus $K$, $t_0$ to $t_\infty$**

Figure 15.4.1 Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of $Q$ and $K$(a) Both $Q$ and $K$ are plotted as points along a number line: the system will always react in the way that causes $Q$ to approach $K$. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

## Note the Pattern

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

## Example 15.4.1

At elevated temperatures, methane ($CH_4$) reacts with water to produce hydrogen and carbon monoxide in what is known as a *steam-reforming* reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If $1.2 \times 10^{-2}$ mol of $CH_4$, $8.0 \times 10^{-3}$ mol of $H_2O$, $1.6 \times 10^{-2}$ mol of CO, and $6.0 \times 10^{-3}$ mol of $H_2$ are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and $H_2$ or to the left to form $CH_4$ and $H_2O$?

**Given:** balanced chemical equation, $K$, amounts of reactants and products, and volume

**Asked for:** direction of reaction

**Strategy:**

**A** Calculate the molar concentrations of the reactants and the products.

**B** Use Equation 15.4.1 to determine $Q$. Compare $Q$ and $K$ to determine in which direction the reaction will proceed.

**Solution:**

**A** We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2}$ mol of $CH_4$ in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

**B** We now compute $Q$ and compare it with $K$:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming $H_2$ and CO at the expense of $H_2O$ and $CH_4$.

Exercise

In the water–gas shift reaction introduced in Example 10, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and $H_2O$, 0.0080 mol of $CO_2$, and 0.012 mol of $H_2$ are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

**Answer:** $Q = 0.96$ ($Q > K$), so the reaction will proceed to the left, and CO and $H_2O$ will form.

## Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that $Q$ no longer equals $K$, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_{3(s)} \rightleftharpoons PbO_{(s)} + CO_{2(g)} \tag{15.4.3}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of $CO_2$ at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 15.4.2, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to $CO_2$ because the amount of $PbCO_3$ is not sufficient to give a $CO_2$ concentration equal to $K$. Thus the left portion of the graph represents a system that is *not* at equilibrium because it contains only $CO_2$(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the $CO_2$ concentration: the graph is a horizontal line. Thus any $CO_2$ concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled *A* in Figure 15.4.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of $CO_2$ ($Q > K$). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting $CO_2$ with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 15.4.3 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled *B* in Figure 15.4.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of $CO_2$ ($Q < K$). To reach

equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form $CO_2$ and solid PbO. The reaction in Equation 15.4.2 will therefore proceed to the right as written, until $[CO_2] = K$.

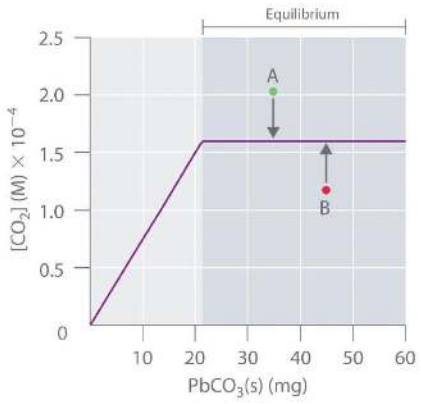



Figure 15.4.2 The Concentration of Gaseous $CO_2$ in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ **Added** Initially the concentration of $CO_2$(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to $CO_2$(g) and solid PbO. Once the $CO_2$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)} \tag{15.4.4}$$

and the equilibrium constant $K$ is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then $[H_2]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of $K$ (Figure 15.4.3). Again, only those pairs of concentrations of $H_2O$ and $H_2$ that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 15.4.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point *A* in Figure 15.4.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction in Equation 15.4.3 will proceed to the right as written, consuming $H_2$ and producing $H_2O$, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point *B* in Figure 15.4.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 15.4.3 will proceed to the left as written, consuming $H_2O$ and producing $H_2$, which causes the concentration ratio to move down and to the right toward the equilibrium line.

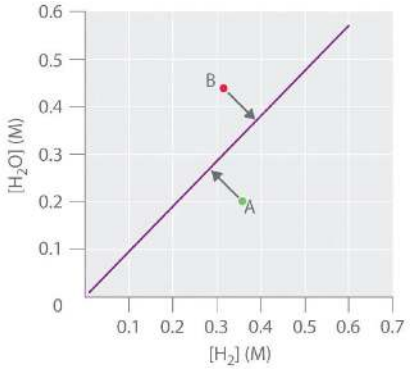



Figure 15.4.3 The Concentration of Water Vapor versus the Concentration of Hydrogen for the CdO(s) + $H_2$(g) ⇌Cd(s) + $H_2O$(g) System at **Equilibrium**For any equilibrium concentration of $H_2O$(g), there is only one equilibrium concentration of $H_2$(g). Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to *K*.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{15.4.5}$$

For this system, $K$ is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of $NH_3$, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 15.4.4. As a result, for a given concentration of either HI or $NH_3$, only a *single* equilibrium composition that contains equal concentrations of both $NH_3$ and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point $A$ in Figure 15.4.4) corresponds to $Q < K$, and the reaction in Equation 15.4.4 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point $B$ in Figure 15.4.3 ) corresponds to $Q > K$, and the reaction in Equation 15.4.4 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

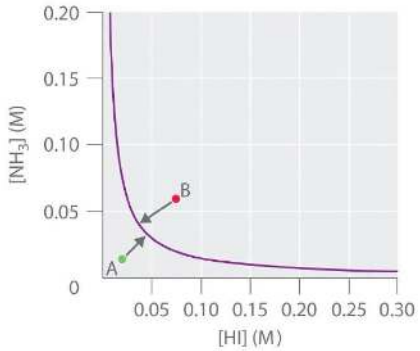



Figure 15.4.4 The Concentration of $NH_3(g)$ versus the Concentration of HI(g) for the $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$ System at **Equilibrium**Only one equilibrium concentration of $NH_3(g)$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large [HI] at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

## Le Chatelier's Principle

When a system at equilibrium is perturbed in some way, the effects of the perturbation can be predicted qualitatively using Le Chatelier's principleIf a stress is applied to a system at equilibrium, the composition of the system will change to relieve the applied stress. (named after the French chemist Henri Louis Le Chatelier, 1850–1936).The name is pronounced "Luh SHOT-lee-ay." This principle can be stated as follows: *if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress.* Stress occurs when any change in a system affects the magnitude of $Q$ or $K$. In Equation 15.4.4, for example, increasing $[NH_3]$ produces a stress on the system that requires a decrease in [HI] for the system to return to equilibrium. As a further example, consider esters, which are one of the products of an equilibrium reaction between a carboxylic acid and an alcohol. (For more information on this type of reaction, see Section 7.5 .) Esters are responsible for the scents we associate with fruits (such as oranges and bananas), and they are also used as scents in perfumes. Applying a stress to the reaction of a carboxylic acid and an alcohol will change the composition of the system, leading to an increase or a decrease in the amount of ester produced. In Section 15.5 and Section 15.6 , we explore how chemists control reactions conditions to affect equilibrium concentrations.

### Note the Pattern

In all reactions, if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress (Le Chatelier's principle).

### Example 15.4.2

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

1. $2HgO(s) \rightleftharpoons 2Hg(l) + \mathbf{O_2(g)}$: the amount of HgO is doubled.
2. $NH_4HS(s) \rightleftharpoons \mathbf{NH_3(g)} + H_2S(g)$: the concentration of $H_2S$ is tripled.
3. ***n*-butane(g)** $\rightleftharpoons$ isobutane(g): the concentration of isobutane is halved.

**Given:** equilibrium systems and changes

**Asked for:** equilibrium constant expressions and effects of changes

**Strategy:**

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

**Solution:**

1. Because HgO(s) and Hg(l) are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of $O_2$ is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of $O_2$, so no compensatory change is necessary.
2. $NH_4HS$ does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding $H_2S$ triples the $H_2S$ concentration, for example, then the $NH_3$ concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals $K$.
3. For this reaction, $K$ = [isobutane]/[*n*-butane], so halving the concentration of isobutane means that the *n*-butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

1. $HBr(g) + NaH(s) \rightleftharpoons NaBr(s) + \mathbf{H_2(g)}$: the concentration of HBr is decreased by a factor of 3.
2. $6Li(s) + \mathbf{N_2(g)} \rightleftharpoons 2Li_3N(s)$: the amount of Li is tripled.
3. $\mathbf{SO_2(g)} + Cl_2(g) \rightleftharpoons SO_2Cl_2(l)$: the concentration of $Cl_2$ is doubled.

**Answer**

1. $K = [H_2]/[HBr]$; $[H_2]$ must decrease by about a factor of 3.
2. $K = 1/[N_2]$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.
3. $K = 1/[SO_2][Cl_2]$; $[SO_2]$ must decrease by about half.

## Summary

The **reaction quotient (*Q* or $Q_p$)** has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium. **Le Chatelier's principle** states that if a stress is applied to a system at equilibrium, the composition of the system will adjust to counteract the stress.

## Key Takeaway

- The reaction quotient ($Q$) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.

## Key Equation

**Reaction quotient**

Equation 15.4.1:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{15.4.1}$$

## Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 15.4.4 and Figure 15.4.4 as your guides, sketch the shape of each graph using appropriate labels.

1. $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
2. $2MgO_{(s)} \rightleftharpoons 2Mg_{(s)} + O_{2(g)}$
3. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$
4. $2PbS_{(s)} + 3O_{2(g)} \rightleftharpoons 2PbO_{(s)} + 2SO_{2(g)}$

2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

   1. $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + \mathbf{H_2O(g)}$: $[CO_2]$ is doubled.
   2. $\mathbf{N_2F_4(g)} \rightleftharpoons 2NF_2(g)$: [NF] is decreased by a factor of 2.
   3. $H_2(g) + I_2(g) \rightleftharpoons \mathbf{2HI(g)}$: $[I_2]$ is doubled.

3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

   1. $CS_2(g) + \mathbf{4H_2(g)} \rightleftharpoons CH_4(g) + 2H_2S(g)$: $[CS_2]$ is doubled.
   2. $\mathbf{PCl_5(g)} \rightleftharpoons PCl_3(g) + Cl_2(g)$: $[Cl_2]$ is decreased by a factor of 2.
   3. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + \mathbf{6H_2O(g)}$: [NO] is doubled.

## Answer

1.
2.
3. 1. $K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$; doubling $[CS_2]$ would require decreasing $[H_2]$ by a factor of $2\sqrt{4} \cong 1.189$.
   2. $K = \frac{[PCl_3]}{[Cl_2][PCl_5]}$; if $[Cl_2]$ is halved, $[PCl_5]$ must also be halved.
   3. $K = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}$; if $[NO]$ is doubled, $[H_2O]$ is multiplied by $22/3 \cong 1.587$.

## Numerical Problems

1. The data in the following table were collected at 450°C for the reaction

   $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

| | Equilibrium Partial Pressure (atm) | | |
|---|---|---|---|
| $P$ (atm) | $NH_3$ | $N_2$ | $H_2$ |
| 30 (equilibrium) | 1.740 | 6.588 | 21.58 |
| 100 | 15.20 | 19.17 | 65.13 |
| 600 | 321.6 | 56.74 | 220.8 |

   The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction 2A ⇌ B + 3 C, $K$ at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

| Experiment | A | B | C |
|---|---|---|---|
| 1 | 2.50 M | 2.50 M | 2.50 M |
| 2 | 1.30 atm | 1.75 atm | 14.15 atm |
| 3 | 12.61 mol | 18.72 mol | 6.51 mol |

3. The following two reactions are carried out at 823 K:

$$CoO_{(s)} + H_{2(g)} \rightleftharpoons Co_{(s)} + H_2O_{(g)} \text{ with } K = 67$$

$$CoO_{(s)} + CO_{(g)} \rightleftharpoons Co_{(s)} + CO_{2(g)} \text{ with } K = 490$$

   1. Write the equilibrium expression for each reaction.
   2. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of $H_2$ or CO plus 0.500 mol CoO.
   3. Using the information provided, calculate $K_p$ for the following reaction: $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$
   4. Describe the shape of the graphs of [reactants] versus [products] as the amount of CoO changes.

4. Hydrogen iodide (HI) is synthesized via $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, for which $K_p = 54.5$ at 425°C. Given a 2.0 L vessel containing $1.12 \times 10^{-2}$ mol of $H_2$ and $1.8 \times 10^{-3}$ mol of $I_2$ at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains $3.64 \times 10^{-1}$ mol of $H_2$. Calculate $Q$ and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

## Answers

1. Not at equilibrium; in both cases, the sum of the equilibrium partial pressures is *less* than the total pressure, so the reaction will proceed to the right to decrease the pressure.
2. 
3. 
   1. $K = [H_2O][H_2]$; K=[CO2][CO]
   2. $P_{H_2O} = 21.0\ atm$; $P_{H_2} = 0.27\ atm$; $P_{CO_2} = 21.3\ atm$; $P_{CO} = 0.07\ atm$
   3. $K_p = 0.14$
   4. The amount of CoO has no effect on the shape of a graph of products versus reactants *as long as some solid CoO is present*.
4. 

## Contributors

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Modified by Joshua B. Halpern

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# 15.5: Factors That Affect Equilibrium

**Learning Objectives**

- To predict the effects of stresses on a system at equilibrium.

Chemists use various strategies to increase the yield of the desired products of reactions. When synthesizing an ester, for example, how can a chemist control the reaction conditions to obtain the maximum amount of the desired product? Only three types of stresses can change the composition of an equilibrium mixture: (1) a change in the concentrations (or partial pressures) of the components by adding or removing reactants or products, (2) a change in the total pressure or volume, and (3) a change in the temperature of the system. In this section, we explore how changes in reaction conditions can affect the equilibrium composition of a system. We will explore each of these possibilities in turn.

## Changes in Concentration

If we add a small volume of carbon tetrachloride ($CCl_4$) solvent to a flask containing crystals of iodine, we obtain a saturated solution of $I_2$ in $CCl_4$, along with undissolved crystals:

$$I_{2(s)} \rightleftharpoons I_{2(soln)} \tag{15.5.1}$$

The system reaches equilibrium, with $K = [I_2]$. If we add more $CCl_4$, thereby diluting the solution, $Q$ is now less than $K$. Le Chatelier's principle tells us that the system will react to relieve the stress—but how? Adding solvent stressed the system by decreasing the concentration of dissolved $I_2$. Hence more crystals will dissolve, thereby increasing the concentration of dissolved $I_2$ until the system again reaches equilibrium if enough solid $I_2$ is available (Figure 15.5.1). By adding solvent, we drove the reaction shown in Equation 15.5.1 to the right as written.

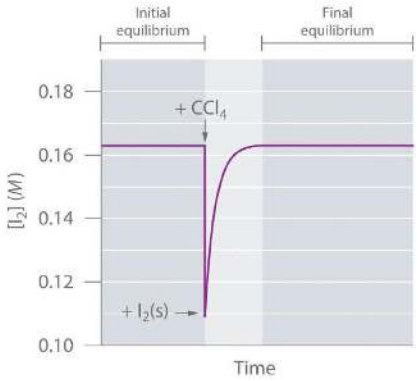



Figure 15.5.1 The Concentration of Dissolved $I_2$ as a Function of Time Following the Addition of More Solvent to a Saturated Solution in Contact with Excess Solid $I_2$ The concentration of $I_2$ decreases initially due to dilution but returns to its original value as long as solid $I_2$ is present.

We encounter a more complex system in the reaction of hydrogen and nitrogen to form ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.5.2}$$

The $K_p$ for this reaction is $2.14 \times 10^{-2}$ at about 540 K. Under one set of equilibrium conditions, the partial pressure of ammonia is $P(NH_3) = 0.454$ atm, that of hydrogen is $P(H_2) = 2.319$ atm, and that of nitrogen is $P(N_2) = 0.773$ atm. If an additional 1 atm of hydrogen is added to the reactor to give $P(H_2) = 3.319$ atm, how will the system respond? Because the stress is an increase in $P(H_2)$ the system must respond in some way that decreases the partial pressure of hydrogen to counteract the stress. The reaction will therefore proceed to the right as written, consuming $H_2$ and $N_2$ and forming additional $NH_3$. Initially, the partial pressures of $H_2$ and $N_2$ will decrease, and the partial pressure of $NH_3$ will increase until the system eventually reaches a new equilibrium composition, which will have a net increase in $P(H_2)$

We can confirm that this is indeed what will happen by evaluating $Q_p$ under the new conditions and comparing its value with $K_p$. The equations used to evaluate $K_p$ and $Q_p$ have the same form: substituting the values after adding hydrogen into the expression for $Q_p$ results in the following:

$$Q_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(0.454)^2}{(0.773)(2.319 + 1.00)^3} = 7.29 \times 10^{-3} \tag{15.5.1}$$

Thus $Q_p < K_p$, which tells us that the ratio of products to reactants is less than at equilibrium. To reach equilibrium, the reaction must proceed to the right as written: the partial pressures of the products will increase, and the partial pressures of the reactants will decrease. $Q_p$ will thereby increase until it equals $K_p$, and the system will once again be at equilibrium. Changes in the partial pressures of the various substances in the reaction mixture (Equation 15.5.2) as a function of time are shown in Figure 15.5.2.

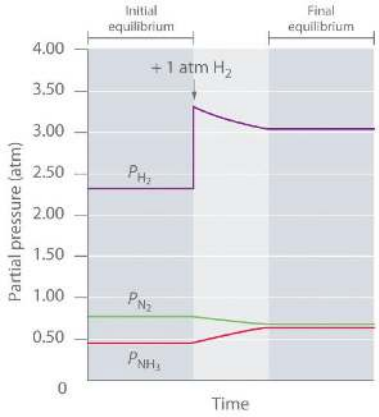



Figure 15.5.2 The Partial Pressures of $H_2$, $N_2$, and $NH_3$ as a Function of Time Following the Addition of More $H_2$ to an Equilibrium **Mixture**Some of the added hydrogen is consumed by reacting with nitrogen to produce more ammonia, allowing the system to reach a new equilibrium composition.

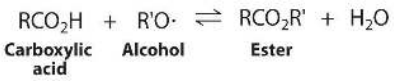
We can force a reaction to go essentially to completion, regardless of the magnitude of $K$, by continually removing one of the products from the reaction mixture. Consider, for example, the *methanation* reaction, in which hydrogen reacts with carbon monoxide to form methane and water:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \tag{15.5.3}$$

This reaction is used for the industrial production of methane, whereas the reverse reaction is used for the production of $H_2$ (Example 14). The expression for $Q$ has the following form:

$$Q = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \tag{15.5.4}$$

Regardless of the magnitude of $K$, if either $H_2O$ or $CH_4$ can be removed from the reaction mixture so that $[H_2O]$ or $[CH_4]$ is approximately zero, then $Q \approx 0$. In other words, when product is removed, the system is stressed ($Q << K$), and more product will form to counter the stress. Because water (bp = 100°C) is much less volatile than methane, hydrogen, or carbon monoxide (all of which have boiling points below −100°C), passing the gaseous reaction mixture through a cold coil will cause the water vapor to condense to a liquid that can be drawn off. Continuing to remove water from the system forces the reaction to the right as the system attempts to equilibrate, thus enriching the reaction mixture in methane. This technique, referred to as *driving a reaction to completion*, can be used to force a reaction to completion even if $K$ is relatively small. For example, esters are usually synthesized by removing water. The products of the condensation reaction are shown here. In Chapter 19, we will describe the thermodynamic basis for the change in the equilibrium position caused by changes in the concentrations of reaction components.




## Example 15.5.1

For each equilibrium system, predict the effect of the indicated stress on the specified quantity.

1. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$:
   (1) the effect of removing $O_2$ on $P(SO_2)$
   (2) the effect of removing $O_2$ on $P(SO_3)$

2. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$:
   (1) the effect of removing $CO_2$ on the amount of $CaCO_3$;
   (2) the effect of adding $CaCO_3$ on $P(CO_2)$

**Given:** balanced chemical equations and changes

**Asked for:** effects of indicated stresses

**Strategy:**

Use $Q$ and $K$ to predict the effect of the stress on each reaction.

**Solution:**

1. (1) Removing $O_2$ will decrease $P(O_2)$thereby decreasing the denominator in the reaction quotient and making $Q_p > K_p$. The reaction will proceed to the left as written, increasing the partial pressures of $SO_2$ and $O_2$ until $Q_p$ once again equals $K_p$.
   (2) Removing $O_2$ will decrease $P(O_2)$ and thus increase $Q_p$, so the reaction will proceed to the left. The partial pressure of $SO_3$ will decrease.
2. $K_p$ and $Q_p$ are both equal to $P(CO_2)$.
   (1) Removing $CO_2$ from the system causes more $CaCO_3$ to react to produce $CO_2$, which increases $P(CO_2)$ to the partial pressure required by $K_p$. (2) Adding (or removing) solid $CaCO_3$ has no effect on $P(CO_2)$ because it does not appear in the expression for $K_p$ (or $Q_p$).

Exercise

For each equilibrium system, predict the effect that the indicated stress will have on the specified quantity.

1. $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$:
   1. the effect of adding $CO$ on $[H_2]$;
   2. the effect of adding $CO_2$ on $[H_2]$
2. $CuO_{(s)} + CO_{(g)} \rightleftharpoons Cu_{(s)} + CO_{2(g)}$:
   1. the effect of adding $CO$ on the amount of $Cu$;
   2. the effect of adding $CO_2$ on $[CO]$

**Answer**

1. (1) $[H_2]$ increases; (2) $[H_2]$ decreases.
2. (1) the amount of Cu increases; (2) [CO] increases.

## Changes in Total Pressure or Volume

Because liquids are relatively incompressible, changing the pressure above a liquid solution has little effect on the concentrations of dissolved substances. Consequently, changes in external pressure have very little effect on equilibrium systems that contain only solids or liquids. In contrast, because gases are highly compressible, their concentrations vary dramatically with pressure. From the ideal gas law, $PV = nRT$, described in Chapter 10, the concentration ($C$) of a gas is related to its pressure as follows:

$$C = \frac{n}{V} = \frac{P}{RT} \tag{15.5.5}$$

Hence the concentration of any gaseous reactant or product is directly proportional to the applied pressure ($P$) and inversely proportional to the total volume ($V$). Consequently, the equilibrium compositions of systems that contain gaseous substances are quite sensitive to changes in pressure, volume, and temperature.

These principles can be illustrated using the reversible dissociation of gaseous $N_2O_4$ to gaseous $NO_2$ (Equation 15.2.1).

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{15.1.1}$$

The syringe shown in Figure 15.5.3 initially contains an equilibrium mixture of colorless $N_2O_4$ and red-brown $NO_2$. Decreasing the volume by 50% causes the mixture to become darker because all concentrations have doubled. Decreasing the volume also constitutes a stress, however, as we can see by examining the effect of a change in volume on $Q$. At equilibrium,

$$Q = K = \frac{[NO_2]^2}{[N_2O_4]} \tag{15.5.6a}$$

If the volume is decreased by half, the concentrations of the substances in the mixture are doubled, so the new reaction quotient is as follows:

$$Q = \frac{(2[NO_2]_i)^2}{2[N_2O_4]_i} = \frac{4([NO_2]_i)^2}{2[N_2O_4]_i} = 2K \tag{15.5.6b}$$

Because $Q$ is now greater than $K$, the system is no longer at equilibrium. The stress can be relieved if the reaction proceeds to the left, consuming 2 mol of $NO_2$ for every 1 mol of $N_2O_4$ produced. This will decrease the concentration of $NO_2$ and increase the concentration of $N_2O_4$, causing $Q$ to decrease until it once again equals $K$. Thus, as shown in part (c) in Figure 15.5.3, the intensity of the brown color due to $NO_2$ decreases with time following the change in volume.






**Figure 15.5.3 The Effect of Changing the Volume (and Thus the Pressure) of an Equilibrium Mixture of $N_2O_4$ and $NO_2$ at Constant Temperature**(a) The syringe with a total volume of 15 mL contains an equilibrium mixture of $N_2O_4$ and $NO_2$; the red-brown color is proportional to the $NO_2$ concentration. (b) If the volume is rapidly decreased by a factor of 2 to 7.5 mL, the initial effect is to double the concentrations of all species present, including $NO_2$. Hence the color becomes more intense. (c) With time,

the system adjusts its composition in response to the stress as predicted by Le Chatelier's principle, forming colorless $N_2O_4$ at the expense of red-brown $NO_2$, which decreases the intensity of the color of the mixture.

### Note the Pattern

Increasing the pressure of a system (or decreasing the volume) favors the side of the reaction that has fewer gaseous molecules and vice versa.

In general, *if a balanced chemical equation contains different numbers of gaseous reactant and product molecules, the equilibrium will be sensitive to changes in volume or pressure*. Increasing the pressure on a system (or decreasing the volume) will favor the side of the reaction that has fewer gaseous molecules and vice versa.

### Example 15.5.2

For each equilibrium system, write the reaction quotient for the system if the pressure is decreased by a factor of 2 (i.e., if the volume is doubled) at constant temperature and then predict the direction of the reaction.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2. $C_2H_{2(g)} + C_2H_{6(g)} \rightleftharpoons 2C_2H_{4(g)}$
3. $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

**Given:** balanced chemical equations

**Asked for:** direction of reaction if pressure is halved

**Strategy:**

Use Le Chatelier's principle to predict the effect of the stress.

**Solution:**

1. Two moles of gaseous products are formed from 4 mol of gaseous reactants. Decreasing the pressure will cause the reaction to shift to the left because that side contains the larger number of moles of gas. Thus the pressure increases, counteracting the stress. $K$ for this reaction is $[NH_3]^2/[N_2][H_2]^3$. When the pressure is decreased by a factor of 2, the concentrations are halved, which means that the new reaction quotient is as follows:

$$Q = \frac{[1/2\ NH_3]^2}{[1/2\ N_2][1/2H_2]^3} = \frac{1/4\ [NH_3]^2}{1/16\ [N_2][H_2]^3} = 4K$$

2. Two moles of gaseous products form from 2 mol of gaseous reactants. Decreasing the pressure will have no effect on the equilibrium composition because both sides of the balanced chemical equation have the same number of moles of gas. Here $K = [C_2H_4]^2/[C_2H_2][C_2H_6]$. The new reaction quotient is as follows:

$$Q = \frac{[C_2H_4]^2}{[C_2H_2][C_2H_6]} = \frac{[1/2C_2H_4]^2}{[1/2C_2H_2][1/2C_2H_6]} = \frac{1/4[C_2H_4]^2}{1/4[C_2H_2][C_2H_6]} = K$$

3. Three moles of gaseous products are formed from 2 mol of gaseous reactants. Decreasing the pressure will favor the side that contains more moles of gas, so the reaction will shift toward the products to increase the pressure. For this reaction $K = [NO]^2[O_2]/[NO_2]^2$. Under the new reaction conditions the reaction quotient is as follows:

$$Q = \frac{[1/2NO]^2[1/2O_2]}{[1/2NO_2]^2} = \frac{1/8[NO]^2[O_2]}{1/4[NO_2]^2} = 1/2K$$

Exercise

For each equilibrium system, write a new reaction quotient for the system if the pressure is increased by a factor of 2 (i.e., if the volume is halved) at constant temperature and then predict the direction in which the reaction will shift.

1. $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$
2. $H_{2(g)} + C_2H_{4(g)} \rightleftharpoons C_2H_{6(g)}$
3. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

**Answer**

1. $Q = K$; no effect
2. $Q = 1/2\ K$; to the right
3. $Q = 1/2\ K$; to the right

## Changes in Temperature

In all the cases we have considered so far, the magnitude of the equilibrium constant, $K$ or $K_p$, was constant. Changes in temperature can, however, change the value of the equilibrium constant without immediately affecting the reaction quotient ($Q \neq K$). In this case, the system is no longer at equilibrium; the composition of the system will change until $Q$ equals $K$ at the new temperature.

To predict how an equilibrium system will respond to a change in temperature, we must know something about the enthalpy change of the reaction ($\Delta H_{rxn}$). As you learned in Chapter 9 , heat is released to the surroundings in an exothermic reaction ($\Delta H_{rxn} < 0$), and heat is absorbed from the surroundings in an endothermic reaction ($\Delta H_{rxn} > 0$). We can express these changes in the following way:

- Exothermic (ΔH<0):

$$\text{reactants} \rightleftharpoons \text{products} + \text{heat} \tag{15.5.7}$$

- Endothermic (ΔH>0):

$$\text{reactants} + \text{heat} \rightleftharpoons \text{products} \tag{15.5.8}$$

Thus heat can be thought of as a product in an exothermic reaction and as a reactant in an endothermic reaction. Increasing the temperature of a system corresponds to adding heat. Le Chatelier's principle predicts that an exothermic reaction will shift to the left (toward the reactants) if the temperature of the system is increased (heat is added). Conversely, an endothermic reaction will shift to the right (toward the products) if the temperature of the system is increased. If a reaction is thermochemically neutral ($\Delta H_{rxn} = 0$), then a change in temperature will not affect the equilibrium composition.

We can examine the effects of temperature on the dissociation of $N_2O_4$ to $NO_2$, for which $\Delta H$ = +58 kJ/mol. This reaction can be written as follows:

$$58\ kJ + N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{15.5.9}$$

Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right, as illustrated in Figure 15.5.4. Thus increasing the temperature increases the ratio of $NO_2$ to $N_2O_4$ at equilibrium, which increases $K$.



Figure 15.5.4 The Effect of Temperature on the Equilibrium between Gaseous $N_2O_4$ and $NO_2$ The value of $K$ changes with temperature of the same 99.9% pure $NO_2/N_2O_4$ sealed in an ampoule. From left to right -196° C, 0° C, 23° C, 35° C, 50° C. In the endothermic reaction , the equilibrium position can be shifted by changing the temperature. When heat is added and the temperature increases, the reaction shifts to the right and the flask turns reddish brown due to an increase in $NO_2$. When heat is removed and the temperature decreases, the reaction shifts to the left and flask turns colorless due to an increase in $N_2O_4$. This demonstrates Le Chatelier's Principle because the equilibrium shifts in the direction that consumes energy. Figure used with permission from Wikipedia.

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: *increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction*. Table 15.5.1 shows the

temperature dependence of the equilibrium constants for the synthesis of ammonia from hydrogen and nitrogen, which is an exothermic reaction with $\Delta H° = -91.8$ kJ/mol. The values of both $K$ and $K_p$ decrease dramatically with increasing temperature, as predicted for an exothermic reaction.

Table 15.5.1 Temperature Dependence of K and $K_p$ for $N_2(g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3(g)$

| Temperature (K) | $K$ | $K_p$ |
|---|---|---|
| 298 | $3.3 \times 10^8$ | $5.6 \times 10^5$ |
| 400 | $3.9 \times 10^4$ | $3.6 \times 10^1$ |
| 450 | $2.6 \times 10^3$ | 1.9 |
| 500 | $1.7 \times 10^2$ | $1.0 \times 10^{-1}$ |
| 550 | $2.6 \times 10^1$ | $1.3 \times 10^{-2}$ |
| 600 | 4.1 | $1.7 \times 10^{-3}$ |

### Note the Pattern

Increasing the temperature causes endothermic reactions to favor products and exothermic reactions to favor reactants.

### Example 15.5.3

For each equilibrium reaction, predict the effect of decreasing the temperature:

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H_{rxn} = -91.8\ \ kJ/mol$
2. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \quad \Delta H_{rxn} = 178\ \ kJ/mol$

**Given:** balanced chemical equations and values of $\Delta H_{rxn}$

**Asked for:** effects of decreasing temperature

**Strategy:**

Use Le Chatelier's principle to predict the effect of decreasing the temperature on each reaction.

**Solution:**

1. The formation of $NH_3$ is exothermic, so we can view heat as one of the products:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 91.8\ kJ$$

2. If the temperature of the mixture is decreased, heat (one of the products) is being removed from the system, which causes the equilibrium to shift to the right. Hence the formation of ammonia is favored at lower temperatures.
3. The decomposition of calcium carbonate is endothermic, so heat can be viewed as one of the reactants:

$$CaCO_{3(s)} + 178\ kJ \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

If the temperature of the mixture is decreased, heat (one of the reactants) is being removed from the system, which causes the equilibrium to shift to the left. Hence the thermal decomposition of calcium carbonate is less favored at lower temperatures.

Exercise

For each equilibrium system, predict the effect of increasing the temperature on the reaction mixture:

1. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ with $\Delta H_{rxn} = -198\ kJ/mol$
2. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ with $\Delta H_{rxn} = +181\ \ kJ/mol$

**Answer**

1. Reaction shifts to the left.
2. Reaction shifts to the right.

## Summary

Three types of stresses can alter the composition of an equilibrium system: adding or removing reactants or products, changing the total pressure or volume, and changing the temperature of the system. A reaction with an unfavorable equilibrium constant can be driven to completion by continually removing one of the products of the reaction. Equilibriums that contain different numbers of gaseous reactant and product molecules are sensitive to changes in volume or pressure; higher pressures favor the side with fewer gaseous molecules. Removing heat from an exothermic reaction favors the formation of products, whereas removing heat from an endothermic reaction favors the formation of reactants.

## Key Takeaway

- Equilibriums are affected by changes in concentration, total pressure or volume, and temperature.

## Conceptual Problems

1. If an equilibrium reaction is endothermic in the forward direction, what is the expected change in the concentration of each component of the system if the temperature of the reaction is increased? If the temperature is decreased?
2. Write the equilibrium equation for the following system:

   \[4NH_{3(g)} +5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}\

   Would you expect the equilibrium to shift toward the products or reactants with an increase in pressure? Why?
3. The reaction rate approximately doubles for every 10°C rise in temperature. What happens to $K$?
4. The formation of $A_2B_2(g)$ via the equilibrium reaction $2AB(g) \rightleftharpoons A_2B_2(g)$ is exothermic. What happens to the ratio $k_f/k_r$ if the temperature is increased? If both temperature and pressure are increased?
5. In each system, predict the effect that the indicated change will have on the specified quantity at equilibrium:
   1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$:

      $H_2$ is removed; what is the effect on $P(I_2)$?
   2. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{2(g)}$

      If $Br_2$ is removed; what is the effect on $P_{NOBr}$?
   3. $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(g)} + CO_{2(g)} + H_2O_{(g)}$

      If $CO_2$ is removed; what is the effect on $P(NaHCO_3)$?
6. What effect will the indicated change have on the specified quantity at equilibrium?
   1. $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

      If $NH_4Cl$ is increased; what is the effect on $P_{HCl}$?
   2. $2H2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$

      If $O_2$ is added; what is the effect on $P(H_2)$?<
   3. $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

      If $Cl_2$ is removed; what is the effect on $P(PCl_5)$?

## Numerical Problems

1. For each equilibrium reaction, describe how $Q$ and $K$ change when the pressure is increased, the temperature is increased, the volume of the system is increased, and the concentration(s) of the reactant(s) is increased.
   1. A(g) ⇌ B(g) Δ H = −20.6 kJ/mol
   2. 2A(g) ⇌ B(g) Δ H = −0.3 kJ/mol
   3. A(g) + B(g) ⇌ 2C(g) Δ H = 46 kJ/mol
2. For each equilibrium reaction, describe how $Q$ and $K$ change when the pressure is decreased, the temperature is increased, the volume of the system is decreased, and the concentration(s) of the reactant(s) is increased.

1. $2A(g) \rightleftharpoons B(g)$ $\Delta H = -80$ kJ/mol
2. $A(g) \rightleftharpoons 2B(g)$ $\Delta H = 0.3$ kJ/mol
3. $2A(g) \rightleftharpoons 2B(g) + C(g)$ $\Delta H = 46$ kJ/mol

3. Le Chatelier's principle states that a system will change its composition to counteract stress. For the system $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, write the equilibrium constant expression $K_p$. What changes in the values of $Q$ and $K$ would you anticipate when (a) the volume is doubled, (b) the pressure is increased by a factor of 2, and (c) $COCl_2$ is removed from the system?
4. For the equilibrium system $3O_2(g) \rightleftharpoons 2\ O_3(g)$, $\Delta H° = 284$ kJ, write the equilibrium constant expression $K_p$. What happens to the values of $Q$ and $K$ if the reaction temperature is increased? What happens to these values if both the temperature and pressure are increased?
5. Carbon and oxygen react to form $CO_2$ gas via $C(s) + O_2(g) \rightleftharpoons CO_2(g)$, for which $K = 1.2 \times 10^{69}$. Would you expect $K$ to increase or decrease if the volume of the system were tripled? Why?
6. The reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2\ (g)$ has $K = 2.2 \times 10^{-10}$ at 100°C. Starting with an initial P( $COCl_2$) of 1.0 atm, you determine the following values of $P_{CO}$ at three successive time intervals: $6.32 \times 10^{-6}$ atm, $1.78 \times 10^{-6}$ atm, and $1.02 \times 10^{-5}$ atm. Based on these data, in which direction will the reaction proceed after each measurement? If chlorine gas is added to the system, what will be the effect on $Q$?
7. The following table lists experimentally determined partial pressures at three temperatures for the reaction $Br_2(g) \rightleftharpoons 2\ Br(g)$

| $T$ (K) | 1123 | 1173 | 1273 |
|---|---|---|---|
| P($Br_2$) (atm) | 3.000 | 0.3333 | $6.755 \times 10^{-2}$ |
| *P(Br)* (atm) | $3.477 \times 10^{-2}$ | $2.159 \times 10^{-2}$ | $2.191 \times 10^{-2}$ |

   Is this an endothermic or an exothermic reaction? Explain your reasoning.
8. The dissociation of water vapor proceeds according to the following reaction:$H_2O(g) \rightleftharpoons 1/2\ O_2(g) + H_2\ (g)$. At 1300 K, there is 0.0027% dissociation, whereas at 2155 K, the dissociation is 1.18%. Calculate $K$ and $K_p$. Is this an endothermic reaction or an exothermic reaction? How do the magnitudes of the two equilibriums compare? Would increasing the pressure improve the yield of $H_2$ gas at either temperature? (Hint: assume that the system initially contains 1.00 mol of $H_2O$ in a 1.00 L container.)
9. When 1.33 mol of $CO_2$ and 1.33 mol of $H_2$ are mixed in a 0.750 L container and heated to 395°C, they react according to the following equation: $CO_2(g) + H_2\ (g) \rightleftharpoons CO(g) + H_2O(g)$ If $K = 0.802$, what are the equilibrium concentrations of each component of the equilibrium mixture? What happens to $K$ if $H_2O$ is removed during the course of the reaction?
10. The equilibrium reaction $H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$ has $K_p = 2.2 \times 10^9$ at 298 K. If you begin with 2.0 mol of $Br_2$ and 2.0 mol of $H_2$ in a 5.0 L container, what is the partial pressure of HBr at equilibrium? What is the partial pressure of $H_2$ at equilibrium? If $H_2$ is removed from the system, what is the effect on the partial pressure of $Br_2$?
11. Iron(II) oxide reacts with carbon monoxide according to the following equation: $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ At 800°C, $K = 0.34$; at 1000°C, $K = 0.40$.
    1. A 20.0 L container is charged with 800.0 g of $CO_2$, 1436 g of FeO, and 1120 g of iron. What are the equilibrium concentrations of all components of the mixture at each temperature?
    2. What are the partial pressures of the gases at each temperature?
    3. If CO were removed, what would be the effect on P($CO_2$) at each temperature?
12. The equilibrium constant $K$ for the reaction $C(s) + CO_2\ g) >\rightleftharpoons 2\ CO(g)$ is 1.9 at 1000 K and 0.133 at 298 K.
    1. If excess C is allowed to react with 25.0 g of $CO_2$ in a 3.00 L flask, how many grams of CO are produced at each temperature?
    2. What are the partial pressures of each gas at 298 K? at 1000 K?
    3. Would you expect $K$ to increase or decrease if the pressure were increased at constant temperature and volume?

13. Data for the oxidation of methane, $CH_4(g) + 2\ O_2(g) \rightleftharpoons CO_2(g) + 2\ H_2O(g)$, in a closed 5.0 L vessel are listed in the following table. Fill in the blanks and determine the missing values of $Q$ and $K$ (indicated by ?) as the reaction is driven to completion.

| | $CH_4$ | $O_2$ | $CO_2$ | $H_2O$ | $Q$ | $K$ |
|---|---|---|---|---|---|---|
| initial (moles) | 0.45 | 0.90 | 0 | 0 | ? | |
| at equilibrium | | | | | | 1.29 |
| add 0.50 mol of methane | 0.95 | | | | ? | |
| new equilibrium | | | | | | ? |
| remove water | | | | 0 | ? | |
| new equilibrium | | | | | | 1.29 |

## Answers

1.
2.
3. $K_p = P(COCl_2)/(P(CO)\ P(Cl_2))\ P$

   None of the changes would affect $K$; (a) $Q$ doubles; (b) $Q$ is halved; $Q$ decreases.

4.
5. $K$ would not change; it does not depend on volume.
6.
7.
8.
9. $[CO] = [H_2O] = 0.839$ M, $[CO_2] = [H_2] = 0.930$ M; no effect on $K$
10.
11. 1. At 800°C, $[CO] = 0.678$ M, $[CO_2] = 0.231$ M; at 1000°C, $[CO] = 0.645$ M, $[CO_2] = 0.264$ M
    2. At 800°C, PCO = 59.7 atm, $P(CO_2) = 20.3$ atm; at 1000°C, $P(CO) = 67.4$ atm, $P(CO_2) = 27.6$ atm.
    3. Removing CO would cause the reaction to shift to the right, causing $P(CO_2)$ to decrease.
12.
13.

| | $CH_4$ | $O_2$ | $CO_2$ | $H_2O$ | $Q$ | $K$ |
|---|---|---|---|---|---|---|
| initial (moles) | 0.45 | 0.90 | 0 | 0 | **0** | 1.29 |
| at equilibrium | 0.215 | 0.43 | 0.235 | 0.47 | $K$ | 1.29 |
| add 0.50 mol of methane | 0.715 | 0.43 | 0.235 | 0.47 | **0.39** | 1.29 |
| new equilibrium | 0.665 | 0.33 | 0.285 | 0.57 | $K$ | **1.29** |
| remove water | 0.665 | 0.33 | 0.285 | 0 | **0** | 1.29 |
| new equilibrium | 0.57 | 0.14 | 0.38 | 0.19 | $K$ | 1.29 |

## Contributors

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# 15.6: Controlling the Products of Reactions

**Learning Objectives**

- To understand different ways to control the products of a reaction.

Whether in the synthetic laboratory or in industrial settings, one of the primary goals of modern chemistry is to control the identity and quantity of the products of chemical reactions. For example, a process aimed at synthesizing ammonia is designed to maximize the amount of ammonia produced using a given amount of energy. Alternatively, other processes may be designed to minimize the creation of undesired products, such as pollutants emitted from an internal combustion engine. To achieve these goals, chemists must consider the competing effects of the reaction conditions that they can control.

One way to obtain a high yield of a desired compound is to make the reaction rate of the desired reaction much faster than the reaction rates of any other possible reactions that might occur in the system. Altering reaction conditions to control reaction rates, thereby obtaining a single product or set of products, is called kinetic controlThe altering of reaction conditions to control reaction rates, thereby obtaining a single desired product or set of products. A second approach, called thermodynamic control. The altering of reaction conditions so that a single desired product or set of products is present in significant quantities at equilibrium., consists of adjusting conditions so that at equilibrium only the desired products are present in significant quantities.

An example of thermodynamic control is the Haber-Bosch process. Karl Bosch (1874–1940) was a German chemical engineer who was responsible for designing the process that took advantage of Fritz Haber's discoveries regarding the $N_2$ + $H_2$/$NH_3$ equilibrium to make ammonia synthesis via this route cost-effective. He received the Nobel Prize in Chemistry in 1931 for his work. The industrial process is called either the Haber process or the Haber-Bosch process. used to synthesize ammonia via the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.6.1a}$$

with

$$\Delta H_{rxn} = -91.8\ kJ/mol \tag{15.6.1b}$$

Because the reaction converts 4 mol of gaseous reactants to only 2 mol of gaseous product, Le Chatelier's principle predicts that the formation of $NH_3$ will be favored when the pressure is increased. The reaction is exothermic, however ($\Delta H_{rxn}$ = −91.8 kJ/mol), so the equilibrium constant decreases with increasing temperature, which causes an equilibrium mixture to contain only relatively small amounts of ammonia at high temperatures (Figure 15.6.1). Taken together, these considerations suggest that the maximum yield of $NH_3$ will be obtained if the reaction is carried out at as low a temperature and as high a pressure as possible. Unfortunately, at temperatures less than approximately 300°C, where the equilibrium yield of ammonia would be relatively high, the reaction is too *slow* to be of any commercial use. The industrial process therefore uses a mixed oxide ($Fe_2O_3$/$K_2O$) catalyst that enables the reaction to proceed at a significant rate at temperatures of 400°C–530°C, where the formation of ammonia is less unfavorable than at higher temperatures.

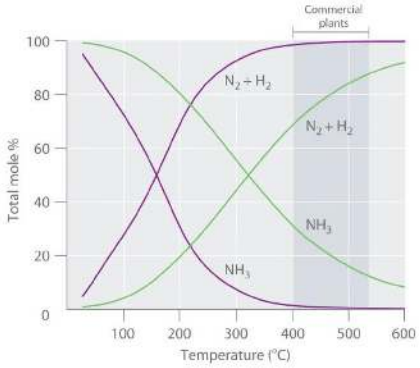



Figure 15.6.1 Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic *decrease* in the proportion of $NH_3$ at equilibrium at higher temperatures in both cases, as well as the large *increase* in the proportion of $NH_3$ at equilibrium at any temperature for the system at higher pressure (green) versus lower pressure (purple). Commercial plants that use the Haber-Bosch process to synthesize ammonia on an industrial scale operate at temperatures of 400°C–530°C (indicated by the darker gray band) and total pressures of 130–330 atm.

Because of the low value of the equilibrium constant at high temperatures (e.g., $K$ = 0.039 at 800 K), there is no way to produce an equilibrium mixture that contains large proportions of ammonia at high temperatures. We can, however, control the temperature and the pressure while using a catalyst to convert a fraction of the $N_2$ and $H_2$ in the reaction mixture to $NH_3$, as is done in the Haber-Bosch process. This process also makes use of the fact that the product—ammonia—is less volatile than the reactants. Because $NH_3$ is a liquid at room temperature at pressures greater than 10 atm, cooling the reaction mixture causes $NH_3$ to condense from the vapor as liquid ammonia, which is easily separated from unreacted $N_2$ and $H_2$. The unreacted gases are recycled until complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure 15.6.2 is a simplified layout of a Haber-Bosch process plant.

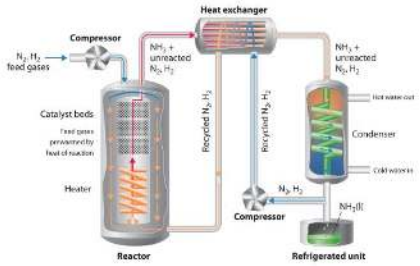



Figure 15.6.2 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process A 3:1 mixture of gaseous $H_2$ and $N_2$ is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an $Fe_2O_3/K_2O$ catalyst, which results in partial conversion to gaseous $NH_3$. The resulting mixture of gaseous $NH_3$, $H_2$, and $N_2$ is passed through a heat exchanger, which uses the hot gases to prewarm recycled $N_2$ and $H_2$, and a condenser to cool the $NH_3$, giving a liquid that is readily separated from unreacted $N_2$ and $H_2$. (Although the normal boiling point of $NH_3$ is −33°C, the boiling point increases rapidly with increasing pressure, to 20°C at 8.5 atm and 126°C at 100 atm.) The unreacted $N_2$ and $H_2$ are recycled to form more $NH_3$.

The Sohio acrylonitrile process, in which propene and ammonia react with oxygen to form acrylonitrile, is an example of a kinetically controlled reaction:

$$CH_2{=}CHCH_{3(g)} + NH_{3(g)} + \tfrac{3}{2}\,O_{2(g)} \rightleftharpoons CH_2{=}CHC{\equiv}N_{(g)} + 3\,H_2O_{(g)} \tag{15.6.2}$$

Like most oxidation reactions of organic compounds, this reaction is highly exothermic ($\Delta H°$ = −519 kJ/mol) and has a very large equilibrium constant ($K$ = 1.2 × $10^{94}$). Nonetheless, the reaction shown in Equation 15.43 is not the reaction a chemist would expect to occur when propene or ammonia is heated in the presence of oxygen. Competing combustion reactions that produce $CO_2$ and $N_2$ from the reactants, such as those shown in Equation 15.6.3 and Equation 15.6.4, are even more exothermic and have even larger equilibrium constants, thereby reducing the yield of the desired product, acrylonitrile:

$$CH_2{=}CHCH_{3(g)} + \tfrac{9}{2}\,O_{2(g)} \rightleftharpoons 3\,CO_{2(g)} + 3\,H_2O_{(g)} \tag{15.6.3a}$$

with

$$\Delta H^\circ = -1926.1\ kJ/mol \tag{15.6.3b}$$

and

$$K = 4.5 \times 10^{338} \tag{15.6.3c}$$

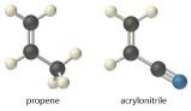
$$2\,NH_{3(g)} + 3\,O_{2(g)} \rightleftharpoons N_{2(g)} + 6\,H_2O_{(g)} \tag{15.6.4a}$$

with

$$\Delta H° = -1359.2\ kJ/mol, \tag{15.6.4c}$$

and

$$K = 4.4 \times 10^{234} \tag{15.6.4c}$$




In fact, the formation of acrylonitrile in Equation 15.6.2. is accompanied by the release of approximately 760 kJ/mol of heat due to partial combustion of propene during the reaction.

The Sohio process uses a catalyst that selectively accelerates the rate of formation of acrylonitrile without significantly affecting the reaction rates of competing combustion reactions. Consequently, acrylonitrile is formed more rapidly than $CO_2$ and $N_2$ under the optimized reaction conditions (approximately 1.5 atm and 450°C). The reaction mixture is rapidly cooled to prevent further oxidation or combustion of acrylonitrile, which is then washed out of the vapor with a liquid water spray. Thus controlling the kinetics of the reaction causes the desired product to be formed under conditions where equilibrium is not established. In industry, this reaction is carried out on an enormous scale. Acrylonitrile is the building block of the polymer called *polyacrylonitrile*, found in all the products referred to collectively as *acrylics*, whose wide range of uses includes the synthesis of fibers woven into clothing and carpets.

## Note the Pattern

Controlling the amount of product formed requires that both thermodynamic and kinetic factors be considered.

## Example 15.6.1

Recall that methanation is the reaction of hydrogen with carbon monoxide to form methane and water:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \tag{15.6.1}$$

This reaction is the reverse of the steam reforming of methane described in Example 14. The reaction is exothermic ($\Delta H°$ = −206 kJ/mol), with an equilibrium constant at room temperature of $K_p = 7.6 \times 10^{24}$. Unfortunately, however, CO and $H_2$ do not react at an appreciable rate at room temperature. What conditions would you select to maximize the amount of methane formed per unit time by this reaction?

**Given:** balanced chemical equation and values of $\Delta H°$ and $K$

**Asked for:** conditions to maximize yield of product

**Strategy:**

Consider the effect of changes in temperature and pressure and the addition of an effective catalyst on the reaction rate and equilibrium of the reaction. Determine which combination of reaction conditions will result in the maximum production of methane.

**Solution:**

The products are highly favored at equilibrium, but the rate at which equilibrium is reached is too slow to be useful. You learned in Chapter 14 that the reaction rate can often be increased dramatically by increasing the temperature of the reactants. Unfortunately, however, because the reaction is quite exothermic, an increase in temperature will shift the equilibrium to the left, causing more reactants to form and relieving the stress on the system by absorbing the added heat. If we increase the temperature too much, the

equilibrium will no longer favor methane formation. (In fact, the equilibrium constant for this reaction is very temperature sensitive, decreasing to only $1.9 \times 10^{-3}$ at 1000°C.) To increase the reaction rate, we can try to find a catalyst that will operate at lower temperatures where equilibrium favors the formation of products. Higher pressures will also favor the formation of products because 4 mol of gaseous reactant are converted to only 2 mol of gaseous product. Very high pressures should not be needed, however, because the equilibrium constant favors the formation of products. Thus optimal conditions for the reaction include carrying it out at temperatures greater than room temperature (but not too high), adding a catalyst, and using pressures greater than atmospheric pressure.

Industrially, catalytic methanation is typically carried out at pressures of 1–100 atm and temperatures of 250°C–450°C in the presence of a nickel catalyst. (At 425°C°C, $K_p$ is $3.7 \times 10^3$, so the formation of products is still favored.) The synthesis of methane can also be favored by removing either $H_2O$ or $CH_4$ from the reaction mixture by condensation as they form.

Exercise

As you learned in Example 10, the water–gas shift reaction is as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \tag{15.6.2}$$

$K_p$ = 0.106 and $\Delta H$ = 41.2 kJ/mol at 700 K. What reaction conditions would you use to maximize the yield of carbon monoxide?

**Answer:** high temperatures to increase the reaction rate and favor product formation, a catalyst to increase the reaction rate, and atmospheric pressure because the equilibrium will not be greatly affected by pressure

## Summary

Changing conditions to affect the reaction rates to obtain a single product is called **kinetic control** of the system. In contrast, **thermodynamic control** is adjusting the conditions to ensure that only the desired product or products are present in significant concentrations at equilibrium.

## Key Takeaway

- Both kinetic and thermodynamic factors can be used to control reaction products.

## Conceptual Problems

1. A reaction mixture will produce either product A or B depending on the reaction pathway. In the absence of a catalyst, product A is formed; in the presence of a catalyst, product B is formed. What conclusions can you draw about the forward and reverse rates of the reaction that produces A versus the reaction that produces B in (a) the absence of a catalyst and (b) the presence of a catalyst?
2. Describe how you would design an experiment to determine the equilibrium constant for the synthesis of ammonia:

   $$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

   The forward reaction is exothermic ($\Delta H°$ = −91.8 kJ). What effect would an increase in temperature have on the equilibrium constant?
3. What effect does a catalyst have on each of the following?
   1. the equilibrium position of a reaction
   2. the rate at which equilibrium is reached
   3. the equilibrium constant?
4. How can the ratio $Q/K$ be used to determine in which direction a reaction will proceed to reach equilibrium?
5. Industrial reactions are frequently run under conditions in which competing reactions can occur. Explain how a catalyst can be used to achieve reaction selectivity. Does the ratio $Q/K$ for the selected reaction change in the presence of a catalyst?

## Numerical Problems

1. The oxidation of acetylene via $2C_2H_2$ (g) + $5O_2$(g) ⇌ 4 $CO_2$(g) + 2 $H_2O$(l) has $\Delta H°$ = −2600 kJ. What strategy would you use with regard to temperature, volume, and pressure to maximize the yield of product?

2. The oxidation of carbon monoxide via $CO(g) + 1/2\ O_2(g) \rightleftharpoons CO_2(g)$ has $\Delta H° = -283$ kJ. If you were interested in maximizing the yield of $CO_2$, what general conditions would you select with regard to temperature, pressure, and volume?
3. You are interested in maximizing the product yield of the system $2SO_2(g) + O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$ $K = 280$ and $\Delta H° = -158$ kJ. What general conditions would you select with regard to temperature, pressure, and volume? If $SO_2$ has an initial concentration of 0.200 M and the amount of $O_2$ is stoichiometric, what amount of $SO_3$ is produced at equilibrium?

## Answer

1. Use low temperature and high pressure (small volume).
2. 
3. 

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# 15.7: Essential Skills 7

**Learning Objectives**

- The quadratic formula

Previous Essential Skills sections introduced many of the mathematical operations you need to solve chemical problems. We now introduce the quadratic formula, a mathematical relationship involving sums of powers in a single variable that you will need to apply to solve some of the problems in this chapter.

## The Quadratic Formula

Mathematical expressions that involve a sum of powers in one or more variables (e.g., $x$) multiplied by coefficients (such as $a$) are called *polynomials*. Polynomials of a single variable have the general form

$$a_n x^n + \ldots + a_2 x^2 + a_1 x + a_0 \tag{15.7.1}$$

The highest power to which the variable in a polynomial is raised is called its *order*. Thus the polynomial shown here is of the *nth* order. For example, if $n$ were 3, the polynomial would be third order.

A *quadratic equation* is a second-order polynomial equation in a single variable $x$:

$$ax^2 + bx + c = 0 \tag{15.7.2}$$

According to the fundamental theorem of algebra, a second-order polynomial equation has two solutions—called *roots*—that can be found using a method called *completing the square*. In this method, we solve for $x$ by first adding $-c$ to both sides of the quadratic equation and then divide both sides by $a$:

$$x^2 + \frac{bx}{a} = -\frac{c}{a} \tag{15.7.3}$$

We can convert the left side of this equation to a perfect square by adding $b^2/4a^2$, which is equal to $(b/2a)^2$:

Left side:

$$x^2 + \frac{b}{a}x + \frac{b^2}{4a^2} = (x + \frac{b}{2a})^2 \tag{15.7.4}$$

Having added a value to the left side, we must now add that same value, $b^2/4a^2$, to the right side:

$$(x + \frac{b}{2a})^2 = -\frac{c}{a} + \frac{b^2}{4a^2} \tag{15.7.5}$$

The common denominator on the right side is $4a^2$. Rearranging the right side, we obtain the following:

$$(x + \frac{b}{2a})^2 = \frac{b^2 - 4ac}{4a^2} \tag{15.7.6}$$

Taking the square root of both sides and solving for $x$,

$$x + \frac{b}{2a} = \frac{\pm\sqrt{b^2 - 4ac}}{2a} \tag{15.7.7}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{15.7.8}$$

This equation, known as the *quadratic formula*, has two roots:

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \tag{15.7.9}$$

and

$$x = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \tag{15.7.10}$$

Thus we can obtain the solutions to a quadratic equation by substituting the values of the coefficients (*a*, *b*, *c*) into the quadratic formula.

When you apply the quadratic formula to obtain solutions to a quadratic equation, it is important to remember that one of the two solutions may not make sense or neither may make sense. There may be times, for example, when a negative solution is not reasonable or when both solutions require that a square root be taken of a negative number. In such cases, we simply discard any solution that is unreasonable and only report a solution that is reasonable. Skill Builder ES1 gives you practice using the quadratic formula.

## Skill Builder ES1

Use the quadratic formula to solve for *x* in each equation. Report your answers to three significant figures.

1. $x^2 + 8x - 5 = 0$
2. $2x^2 - 6x + 3 = 0$
3. $3x^2 - 5x - 4 = 6$
4. $2x(-x + 2) + 1 = 0$
5. $3x(2x + 1) - 4 = 5$

**Solution:**

1. $9x = -8 + 82 - 4(1)(-5)\sqrt{}2(1) = 0.583$ and $x = -8 - 82 - 4(1)(-5)\sqrt{}2(1) = -8.58$
2. $x = -(-6) + (-62) - 4(2)(3)\sqrt{}2(2) = 2.37$ and $x = -(-6) - (-62) - 4(2)(3)\sqrt{}2(2) = 0.634$
3. $x = -(-5) + (-52) - 4(3)(-10)\sqrt{}2(3) = 2.84$ and $x = -(-5) - (-52) - 4(3)(-10)\sqrt{}2(3) = -1.17$
4. $x = -4 + 42 - 4(-2)(1)\sqrt{}2(-2) = -0.225$ and $x = -4 - 42 - 4(-2)(1)\sqrt{}2((-2)) = 2.22$
5. $x = -1 + 12 - 4(2)(-3)\sqrt{}2(2) = 1.00$ and $x = -1 - 12 - 4(2)(-3)\sqrt{}2(2) = 1.50$

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# CHAPTER OVERVIEW

## 16: Aqueous Acid–Base Equilibriums


16.1: The Autoionization of Water
16.2: A Qualitative Description of Acid-Base Equilibria
16.3: Molecular Structure and Acid-Base Strength
16.4: Quantitative Aspects of Acid-Base Equilibria
16.5: Acid-Base Titrations
16.6: Buffers


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# 16.1: The Autoionization of Water

**Learning Objectives**

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and p$K_w$.

As you learned in Chapter 8 and Chapter 4, acids and bases can be defined in several different ways (Table 16.1.1 ). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce $H^+$ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce $OH^-$ (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can *donate* a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can *accept* a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton, as we demonstrated in Chapter 8 . Consequently, all Brønsted–Lowry acid–base reactions actually involve *two* conjugate acid–base pairs and the transfer of a *proton* from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, discussed in Chapter 8, focuses on accepting or donating *pairs of electrons* rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

**Table 16.1.1 Definitions of Acids and Bases**

| | Acids | Bases |
|---|---|---|
| Arrhenius | $H^+$ donor | $OH^-$ donor |
| Brønsted–Lowry | $H^+$ donor | $H^+$ acceptor |
| Lewis | electron-pair acceptor | electron-pair donor |

Because this chapter deals with acid–base equilibriums in *aqueous solution*, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

In Chapter 8, we also introduced the acid–base properties of water, its *autoionization reaction*, and the definition of pH. The purpose of this section is to review those concepts and describe them using the concepts of chemical equilibrium developed in Chapter 15 .

## Acid–Base Properties of Water

The structure of the water molecule, with its polar O–H bonds and two lone pairs of electrons on the oxygen atom, was described in Chapter 8 and Chapter 4, and the structure of liquid water was discussed in Chapter 13 . Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions ($Cl^-$) and protons ($H^+$). As you learned in Chapter 8, the proton, in turn, reacts with a water molecule to form the *hydronium ion* ($H_3O^+$):

$$\underset{\text{aicd}}{HCl_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightarrow \underset{\text{acid}}{H_3O^+_{(aq)}} + \underset{\text{base}}{Cl^-_{(aq)}} \tag{16.1.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an $H^+$ ion. The reaction in Equation 16.1.1 is often written in a simpler form by removing $H_2O$ from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{16.1.2}$$

In Equation 16.1.2, the hydronium ion is represented by $H^+$, although free $H^+$ ions do not exist in liquid water.

Water can also act as an acid, as shown in Equation 16.1.3. In this equilibrium reaction, $H_2O$ donates a proton to $NH_3$, which acts as a base:

$$\underset{acid}{H_2O_{(aq)}} + \underset{base}{NH_{3(aq)}} \rightleftharpoons \underset{acid}{NH^+_{4(aq)}} + \underset{base}{OH^-_{(aq)}} \tag{16.1.3}$$

Thus water is amphiproticSubstances that can behave as either an acid or a base in a chemical reaction, depending on the nature of the other reactant(s)., meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 16.3 is an equilibrium reaction as indicated by the double arrow.

## The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an $OH^-$ ion and an $H_3O^+$ ion in an autoionization process:

$$2H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{16.1.4}$$

The equilibrium constant *K* for this reaction can be written as follows:

$$K = \frac{[H_3O^+(aq)][OH^-(aq)]}{[H_2O(l)]^2} \tag{16.1.5}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25°C, the concentrations of the hydronium ion and the hydroxide ion are equal: $[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}$ M. Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb. We can calculate $[H_2O]$ at 25°C from the density of water at this temperature (0.997 g/mL):

$$[H_2O(l)] = mol/L = (0.997 \ \cancel{g}/mL)\left(\frac{1 \ mol}{18.02 \ \cancel{g}}\right)\left(\frac{1000 \ \cancel{mL}}{L}\right) = 55.3 \ M \tag{16.1.6}$$

With so few water molecules dissociated, the equilibrium of the autoionization reaction (Equation 16.4) lies far to the left. Consequently, $[H_2O]$ is essentially unchanged by the autoionization reaction and can be treated as a constant. Incorporating this constant into the equilibrium expression allows us to rearrange Equation 16.1.5 to define a new equilibrium constant, the ion-product constant of liquid water ($K_w$)

$$K = \frac{K_w}{[H_2O(l)]^2} \tag{16.1.7a}$$

with

$$K_w = [H_3O^+(aq)][OH^-(aq)] = [H_3O^+(aq)][OH^-(aq)] \tag{16.1.7b}$$

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25°C into this expression,

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{16.1.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ M. Like any other equilibrium constant, $K_w$ varies with temperature, ranging from $1.15 \times 10^{-15}$ at 0°C to $4.99 \times 10^{-13}$ at 100°C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the $H_3O^+$ concentration is a quantitative measure of acidity: the higher the $H_3O^+$ concentration, the more acidic the solution. Conversely, the higher the $OH^-$ concentration, the more basic the solution. In most situations that you will encounter, the $H_3O^+$ and $OH^-$ concentrations from the dissociation of water are so small ($1.003 \times 10^{-7}$ M) that they can be ignored in calculating the $H_3O^+$ or $OH^-$ concentrations of solutions of acids and bases, but this is not always the case.

## The Relationship among pH, pOH, and p$K_w$

The *pH scale* is a concise way of describing the $H_3O^+$ concentration and hence the acidity or basicity of a solution. Recall from Chapter 8 that pH and the $H^+$ ($H_3O^+$) concentration are related as follows:

$$pH = -log_{10}[H^+(aq)] \tag{16.1.9}$$

$$[H^+(aq)] = 10^{-pH} \tag{16.1.10}$$

Because the scale is logarithmic, a pH difference of *1* between two solutions corresponds to a difference of a factor of *10* in their hydronium ion concentrations. (Refer to Essential Skills 3 in Section 8.11 , if you need to refresh your memory about how to use logarithms.) Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}$ M), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous *pOH scale* to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -log_{10}[OH^-(aq)] \tag{16.1.11}$$

$$[OH^-(aq)] = 10^{-pOH} \tag{16.1.12}$$

The constant $K_w$ can also be expressed using this notation, where $pK_w = -\log K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25°C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for *any* aqueous solution at 25°C by taking the negative logarithm of both sides of Equation 16.7:

$$\begin{aligned} -logKw &= -log([H_3O^+(aq)][OH-(aq)]) \\ &= (-log[H_3O^+(aq)]) + (-log[OH^-(aq)]) = pH + pOH \end{aligned} \tag{16.1.13}$$

Thus at any temperature, pH + pOH = $pK_w$, so at 25°C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the $pK_w$ at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 16.1.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

### Note the Pattern

For any neutral solution, pH + pOH = 14.00 (at 25°C) and and pH=12pKw.

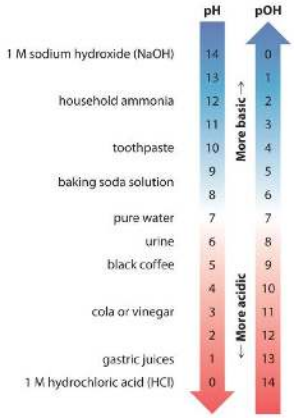



Figure 16.1.1 The Inverse Relationship between the pH and pOH **Scales**As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

### Example 16.1.1

The $K_w$ for water at 100°C is $4.99 \times 10^{-13}$. Calculate $pK_w$ for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100°C. Report pH and pOH values to two decimal places.

**Given:** $K_w$

**Asked for:** $pK_w$, pH, and pOH

**Strategy:**

**A** Calculate p$K_w$ by taking the negative logarithm of $K_w$.

**B** For a neutral aqueous solution, [$H_3O^+$] = [$OH^-$]. Use this relationship and Equation 16.7 to calculate [$H_3O^+$] and [$OH^-$]. Then determine the pH and the pOH for the solution.

**Solution:**

**A** Because p$K_w$ is the negative logarithm of $K_w$, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: $K_w$ is between $10^{-13}$ and $10^{-12}$, so p$K_w$ must be between 12 and 13.

**B** Equation 16.1.7 shows that $K_w$ = [$H_3O^+$][$OH^-$]. Because [$H_3O^+$] = [$OH^-$] in a neutral solution, we can let $x$ = [$H_3O^+$] = [$OH^-$]:

$$K_w = [H_3O^+][OH^-] = (x)(x) = x^2$$

$$x = \sqrt{K_w} = \sqrt{4.99 \times 10^{-13}} = 7.06 \times 10^{-7}\ M$$

Because $x$ is equal to both [$H_3O^+$] and [$OH^-$],

pH = pOH = −log(7.06 × $10^{-7}$) = 6.15 (to two decimal places)

We could obtain the same answer more easily (without using logarithms) by using the p$K_w$. In this case, we know that p$K_w$ = 12.302, and from Equation 16.13, we know that p$K_w$ = pH + pOH. Because pH = pOH in a neutral solution, we can use Equation 16.13 directly, setting pH = pOH = $y$. Solving to two decimal places we obtain the following:

$$pK_w pH + pOH = y + y = 2y$$

$$y = \frac{pK_w}{2} = \frac{12.302}{2} = 6.15 = pH = pOH$$

Exercise

Humans maintain an internal temperature of about 37°C. At this temperature, $K_w$ = 3.55 × $10^{-14}$. Calculate p$K_w$ and the pH and the pOH of a neutral solution at 37°C. Report pH and pOH values to two decimal places.

**Answer:** p$K_w$ = 13.45 pH = pOH = 6.73

## Summary

Water is **amphiprotic**: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion ($H_3O^+$). The *autoionization* of liquid water produces $OH^-$ and $H_3O^+$ ions. The equilibrium constant for this reaction is called the **ion-product constant of liquid water ($K_w$)** and is defined as $K_w$ = [$H_3O^+$][$OH^-$]. At 25°C, $K_w$ is 1.01 × $10^{-14}$; hence pH + pOH = p$K_w$ = 14.00.

## Key Takeaway

- For any neutral solution, pH + pOH = 14.00 (at 25°C) and pH = 1/2 p$K_w$.

## Key Equations

**Ion-product constant of liquid water**

Equation 16.1.7: $K_w$ = [$H_3O^+$][$OH^-$]

**Definition of pH**

Equation 16.1.9: pH = $-\log_{10}$[$H^+$]

Equation 16.1.10: [$H^+$] = $10^{-pH}$

**Definition of pOH**

Equation 16.1.11: pOH = $-\log_{10}$[$OH^+$]

Equation 16.1.12: [$OH^-$] = $10^{-pOH}$

**Relationship among pH, pOH, and p $K_w$**

Equation 16.1.13: $pK_w = pH + pOH$

## Conceptual Problems

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water ($K_w$)?
2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause $K_w$ to increase or decrease? Why?
3. Show that water is amphiprotic by writing balanced chemical equations for the reactions of water with $HNO_3$ and $NH_3$. In which reaction does water act as the acid? In which does it act as the base?
4. Write a chemical equation for each of the following.
    1. Nitric acid is added to water.
    2. Potassium hydroxide is added to water.
    3. Calcium hydroxide is added to water.
    4. Sulfuric acid is added to water.
5. Show that $K$ for the sum of the following reactions is equal to $K_w$.
    1. $$HMnO_{4(aq)} \rightleftharpoons H^+_{(aq)} + MnO^-_{4(aq)}$$
    2.

## Answers

1. $$K_{auto} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$
$$K_w = [H_3O^+][OH^-] = K_{auto}[H_2O]^2$$
2.
3. water is the base:
$$H_2O_{(l)} + HNO_{3(g)} \rightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$
water is the acid:
$$H_2O_{(l)} + NH_{3(g)} \rightarrow OH^-_{(aq)} + NH^-_{4(aq)}$$
4.
5.

## Numerical Problems

1. The autoionization of sulfuric acid can be described by the following chemical equation:
$$H_2SO_{4(l)} + H_2SO_{4(l)} \rightleftharpoons H_3SO^+_{4(soln)} + H_SO^-_{4(soln)}$$
At 25°C, $K = 3 \times 10^{-4}$. Write an equilibrium constant expression for K($H_2SO_4$) that is analogous to $K_w$. The density of $H_2SO_4$ is 1.8 g/cm$^3$ at 25°C. What is the concentration of $H_3SO_4^+$? What fraction of $H_2SO_4$ is ionized?
2. An aqueous solution of a substance is found to have $[H_3O]^+ = 2.48 \times 10^{-8}$ M. Is the solution acidic, neutral, or basic?
3. The pH of a solution is 5.63. What is its pOH? What is the $[OH^-]$? Is the solution acidic or basic?
4. State whether each solution is acidic, neutral, or basic.
    1. $[H_3O^+] = 8.6 \times 10^{-3}$ M
    2. $[H_3O^+] = 3.7 \times 10^{-9}$ M

3. $[H_3O^+] = 2.1 \times 10^{-7}$ M
4. $[H_3O^+] = 1.4 \times 10^{-6}$ M

5. Calculate the pH and the pOH of each solution.

    1. 0.15 M HBr
    2. 0.03 M KOH
    3. $2.3 \times 10^{-3}$ M $HNO_3$
    4. $9.78 \times 10^{-2}$ M NaOH
    5. 0.00017 M HCl
    6. 5.78 M HI

6. Calculate the pH and the pOH of each solution.

    1. 25.0 mL of $2.3 \times 10^{-2}$ M HCl, diluted to 100 mL
    2. 5.0 mL of 1.87 M NaOH, diluted to 125 mL
    3. 5.0 mL of 5.98 M HCl added to 100 mL of water
    4. 25.0 mL of 3.7 M $HNO_3$ added to 250 mL of water
    5. 35.0 mL of 0.046 M HI added to 500 mL of water
    6. 15.0 mL of 0.0087 M KOH added to 250 mL of water.

7. The pH of stomach acid is approximately 1.5. What is the $[H^+]$?

8. Given the pH values in parentheses, what is the $[H^+]$ of each solution?

    1. household bleach (11.4)
    2. milk (6.5)
    3. orange juice (3.5)
    4. seawater (8.5)
    5. tomato juice (4.2)

9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?

10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

## Answers

1. $$K_{H_2SO_4} = [H_3SO_4^+][HSO_4^-] = K[H_2SO_4]_2$$

   $$[H_3SO_4^+] = 0.3M$$

   $[H_3SO_4^+]$ = 0.3 M; the fraction ionized is 0.02.

2.

3. pOH = 8.37; $[OH^-] = 4.3 \times 10^{-9}$ M; acidic

4.

5. 1. pH = 0.82; pOH = 13.18
   2. pH = 12.5; pOH = 1.5
   3. pH = 2.64; pOH = 11.36
   4. pH = 12.990; pOH = 1.010
   5. pH = 3.77; pOH = 10.23
   6. pH = −0.762; pOH = 14.762

6.

7.

8.

9. 2.9 mg HCl

10.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 16.2: A Qualitative Description of Acid-Base Equilibria

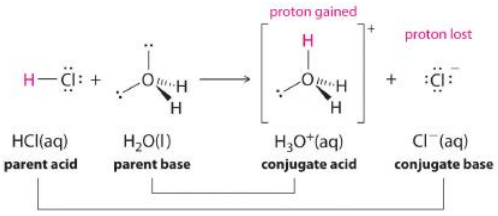
**Learning Objectives**

- To understand the concept of conjugate acid–base pairs.
- To know the relationship between acid or base strength and the magnitude of $K_a$, $K_b$, $pK_a$, and $pK_b$.
- To understand the leveling effect.

We now turn our attention to acid–base reactions to see how the concepts of chemical equilibrium and equilibrium constants can deepen our understanding of this kind of chemical behavior. We begin with a qualitative description of acid–base equilibriums in terms of the Brønsted–Lowry model and then proceed to a quantitative description in Section 16.4 .

## Conjugate Acid–Base Pairs

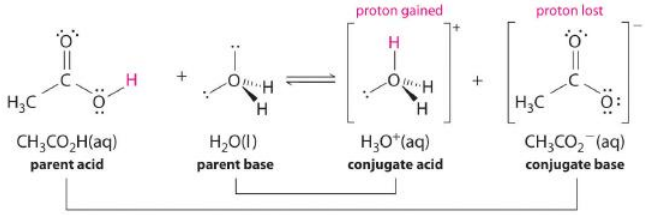
In aqueous solutions, acids and bases can be defined in terms of the transfer of a proton from an acid to a base. Thus for every acidic species in an aqueous solution, there exists a species derived from the acid by the loss of a proton. These two species that differ by only a proton constitute a conjugate acid–base pair. For example, in the reaction of HCl with water (Equation 16.1.1), HCl, the *parent acid*, donates a proton to a water molecule, the *parent base*, thereby forming $Cl^-$. Thus HCl and $Cl^-$ constitute a conjugate acid–base pair. By convention, we always write a conjugate acid–base pair as the acid followed by its conjugate base. In the reverse reaction, the $Cl^-$ ion in solution acts as a base to accept a proton from $H_3O^+$, forming $H_2O$ and HCl. Thus $H_3O^+$ and $H_2O$ constitute a second conjugate acid–base pair. In general, any acid–base reaction must contain *two* conjugate acid–base pairs, which in this case are $HCl/Cl^-$ and $H_3O^+/H_2O$.




### Note the Pattern

All acid–base reactions contain *two* conjugate acid–base pairs.

Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, $H_3O^+$ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and the parent base and its conjugate acid ($H_3O^+/H_2O$).




In the reaction of ammonia with water to give ammonium ions and hydroxide ions (Equation 16.1.3), ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $NH_4^+/NH_3$ and $H_2O/OH^-$. Some common conjugate acid–base pairs are shown in Figure 16.2.1.

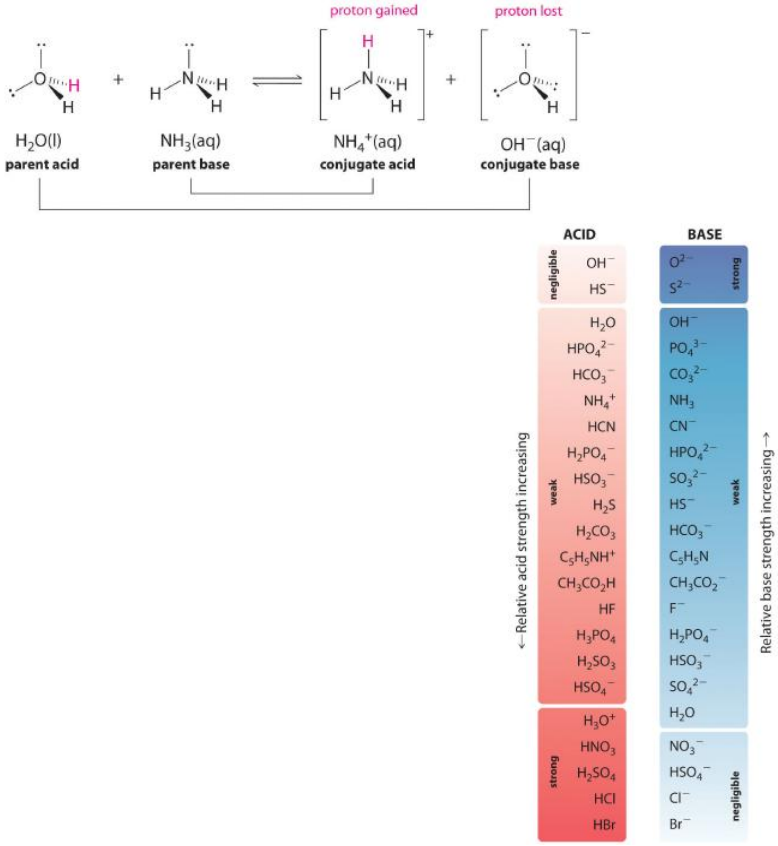



Figure 16.2.1 The Relative Strengths of Some Common Conjugate Acid–Base **Pairs** The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

## Acid–Base Equilibrium Constants: $K_a$, $K_b$, p$K_a$, and p$K_b$

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and $A^-$ is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{16.2.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{16.2.2}$$

As we noted earlier, the concentration of water is essentially constant for all reactions in aqueous solution, so $[H_2O]$ in Equation 16.2.2 can be incorporated into a new quantity, the acid ionization constant ($K_a$)An equilibrium constant for the ionization (dissociation) of a weak acid (HA) with water, HA(aq) + $H_2O$(l) ⇌ $H_3O(aq)^+$ + $A^-$(aq), in which the concentration of water is treated as a constant: Ka = $[H_3O(aq)^+][A^-(aq)]/[HA]$, also called the *acid dissociation constant*:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \tag{16.2.3}$$

Thus the numerical values of $K$ and $K_a$ differ by the concentration of water (55.3 M). Again, for simplicity, $H_3O^+$ can be written as $H^+$ in Equation 16.2.3. Keep in mind, though, that free $H^+$ does not exist in aqueous solutions and that a proton is transferred to $H_2O$ in all acid ionization reactions to form $H_3O^+$. The larger the $K_a$, the stronger the acid and the higher the $H^+$ concentration at equilibrium.Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the *activities* of $H^+$ or $OH^-$, thus making them unitless. The values of $K_a$ for a number of common acids are given in Table 16.2.1.

**Table 16.2.1 Values of $K_a$, p$K_a$, $K_b$, and p$K_b$ for Selected Acids (HA) and Their Conjugate Bases ($A^-$)**

| Acid | HA | $K_a$ | p$K_a$ | $A^-$ | $K_b$ | p$K_b$ |
|---|---|---|---|---|---|---|
| hydroiodic acid | HI | $2 \times 10^{9}$ | −9.3 | $I^-$ | $5.5 \times 10^{-24}$ | 23.26 |
| sulfuric acid (1)* | $H_2SO_4$ | $1 \times 10^{2}$ | −2.0 | $HSO_4^-$ | $1 \times 10^{-16}$ | 16.0 |
| nitric acid | $HNO_3$ | $2.3 \times 10^{1}$ | −1.37 | $NO_3^-$ | $4.3 \times 10^{-16}$ | 15.37 |
| hydronium ion | $H_3O^+$ | 1.0 | 0.00 | $H_2O$ | $1.0 \times 10^{-14}$ | 14.00 |
| sulfuric acid (2)* | $HSO_4^-$ | $1.0 \times 10^{-2}$ | 1.99 | $SO_4^{2-}$ | $9.8 \times 10^{-13}$ | 12.01 |
| hydrofluoric acid | HF | $6.3 \times 10^{-4}$ | 3.20 | $F^-$ | $1.6 \times 10^{-11}$ | 10.80 |
| nitrous acid | $HNO_2$ | $5.6 \times 10^{-4}$ | 3.25 | $NO_2^-$ | $1.8 \times 10^{-11}$ | 10.75 |
| formic acid | $HCO_2H$ | $1.78 \times 10^{-4}$ | 3.750 | $HCO_2^-$ | $5.6 \times 10^{-11}$ | 10.25 |
| benzoic acid | $C_6H_5CO_2H$ | $6.3 \times 10^{-5}$ | 4.20 | $C_6H_5CO_2^-$ | $1.6 \times 10^{-10}$ | 9.80 |
| acetic acid | $CH_3CO_2H$ | $1.7 \times 10^{-5}$ | 4.76 | $CH_3CO_2^-$ | $5.8 \times 10^{-10}$ | 9.24 |
| pyridinium ion | $C_5H_5NH^+$ | $5.9 \times 10^{-6}$ | 5.23 | $C_5H_5N$ | $1.7 \times 10^{-9}$ | 8.77 |
| hypochlorous acid | HOCl | $4.0 \times 10^{-8}$ | 7.40 | $OCl^-$ | $2.5 \times 10^{-7}$ | 6.60 |
| hydrocyanic acid | HCN | $6.2 \times 10^{-10}$ | 9.21 | $CN^-$ | $1.6 \times 10^{-5}$ | 4.79 |
| ammonium ion | $NH_4^+$ | $5.6 \times 10^{-10}$ | 9.25 | $NH_3$ | $1.8 \times 10^{-5}$ | 4.75 |
| water | $H_2O$ | $1.0 \times 10^{-14}$ | 14.00 | $OH^-$ | 1.00 | 0.00 |
| acetylene | $C_2H_2$ | $1 \times 10^{-26}$ | 26.0 | $HC_2^-$ | $1 \times 10^{12}$ | −12.0 |
| ammonia | $NH_3$ | $1 \times 10^{-35}$ | 35.0 | $NH_2^-$ | $1 \times 10^{21}$ | −21.0 |

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and $BH^+$ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{16.2.4}$$

The equilibrium constant for this reaction is the base ionization constant ($K_b$)An equilibrium constant for the reaction of a weak base (B) with water, B(aq) + $H_2O$(l) ⇌ $BH^+$(aq) + $OH^-$(aq), in which the concentration of water is treated as a constant: Kb = $[BH^+][OH^-]/[B]$, also called the *base dissociation constant*:

$$K_b = K[H_2O] = [BH^+][OH^-][B] \tag{16.2.5}$$

Once again, the concentration of water is constant, so it does not appear in the equilibrium constant expression; instead, it is included in the $K_b$. The larger the $K_b$, the stronger the base and the higher the $OH^-$ concentration at equilibrium. The values of $K_b$ for a number of common weak bases are given in Table 16.2.2

**Table 16.2.2 Values of $K_b$, p$K_b$, $K_a$, and p$K_a$ for Selected Weak Bases (B) and Their Conjugate Acids ($BH^+$)**

| Base | B | $K_b$ | p$K_b$ | $BH^+$ | $K_a$ | p$K_a$ |
|---|---|---|---|---|---|---|
| hydroxide ion | $OH^-$ | 1.0 | 0.00* | $H_2O$ | $1.0 \times 10^{-14}$ | 14.00 |
| phosphate ion | $PO_4^{3-}$ | $2.1 \times 10^{-2}$ | 1.68 | $HPO_4^{2-}$ | $4.8 \times 10^{-13}$ | 12.32 |
| dimethylamine | $(CH_3)_2NH$ | $5.4 \times 10^{-4}$ | 3.27 | $(CH_3)_2NH_2^+$ | $1.9 \times 10^{-11}$ | 10.73 |
| methylamine | $CH_3NH_2$ | $4.6 \times 10^{-4}$ | 3.34 | $CH_3NH_3^+$ | $2.2 \times 10^{-11}$ | 10.66 |
| trimethylamine | $(CH_3)_3N$ | $6.3 \times 10^{-5}$ | 4.20 | $(CH_3)_3NH^+$ | $1.6 \times 10^{-10}$ | 9.80 |
| ammonia | $NH_3$ | $1.8 \times 10^{-5}$ | 4.75 | $NH_4^+$ | $5.6 \times 10^{-10}$ | 9.25 |
| pyridine | $C_5H_5N$ | $1.7 \times 10^{-9}$ | 8.77 | $C_5H_5NH^+$ | $5.9 \times 10^{-6}$ | 5.23 |
| aniline | $C_6H_5NH_2$ | $7.4 \times 10^{-10}$ | 9.13 | $C_6H_5NH_3^+$ | $1.3 \times 10^{-5}$ | 4.87 |
| water | $H_2O$ | $1.0 \times 10^{-14}$ | 14.00 | $H_3O^+$ | 1.0* | 0.00 |

*As in Table 16.2.

There is a simple relationship between the magnitude of $K_a$ for an acid and $K_b$ for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of $CN^-$ with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{16.2.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{16.2.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{16.2.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{16.2.9}$$

If we add Equation 16.2.8 and Equation 16.2.9, we obtain the following (recall from Chapter 15 that the equilibrium constant for the *sum* of two reactions is the *product* of the equilibrium constants for the individual reactions):

$$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}} \quad K_a = [H^+]\,\cancel{[CN^-]} / \cancel{[HCN]}$$

$$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}} \quad K_b = [OH^-]\,\cancel{[HCN]} / \cancel{[CN^-]}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-]$$

In this case, the sum of the reactions described by $K_a$ and $K_b$ is the equation for the autoionization of water, and the product of the two equilibrium constants is $K_w$:

$$K_aK_b = K_w \tag{16.2.10}$$

Thus if we know either $K_a$ for an acid or $K_b$ for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and p$K_w$, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining p$K_a$ as follows:

$$pKa = -\log_{10} K_a \tag{16.2.11}$$

$$K_a = 10^{-pK_a} \tag{16.2.12}$$

and $pK_b$ as

$$pK_b = -\log_{10} K_b \tag{16.2.13}$$

$$K_b = 10^{-pK_b} \tag{16.2.14}$$

Similarly, Equation 16.2.10, which expresses the relationship between $K_a$ and $K_b$, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{16.2.15}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{16.2.16}$$

The values of p$K_a$ and p$K_b$ are given for several common acids and bases in Table 16.2.1 and Table 16.2.2 , respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of p$K_a$ correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid ($HNO_2$), with a p$K_a$ of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a p$K_a$ of 9.21. Conversely, smaller values of p$K_b$ correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.2.1 . The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of p$K_a$. This order corresponds to decreasing strength of the conjugate base or increasing values of p$K_b$. At the bottom left of Figure 16.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

### Note the Pattern

The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: *an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows*:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce $H_3O^+$ and $Cl^-$; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{16.2.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of $H_3O^+$ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

### Note the Pattern

All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

### Example 16.2.1

1. Calculate $K_b$ and p$K_b$ of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The p$K_a$ of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

2. Calculate $K_a$ and p$K_a$ of the dimethylammonium ion [$(CH_3)_2NH_2^+$]. The base ionization constant $K_b$ of dimethylamine [$(CH_3)_2NH$] is $5.4 \times 10^{-4}$ at 25°C.

**Given:** p$K_a$ and $K_b$

**Asked for:** corresponding $K_b$ and p$K_b$, $K_a$ and p$K_a$

**Strategy:**

The constants $K_a$ and $K_b$ are related as shown in Equation 16.2.10. The p$K_a$ and p$K_b$ for an acid and its conjugate base are related as shown in Equation 16.2.15 and Equation 16.2.16. Use the relationships p$K$ = −log $K$ and $K = 10^{-pK}$ (Equation 16.24 and Equation 16.26) to convert between $K_a$ and p$K_a$ or $K_b$ and p$K_b$.

**Solution:**

1. We are given the p$K_a$ for butyric acid and asked to calculate the $K_b$ and the p$K_b$ for its conjugate base, the butyrate ion. Because the p$K_a$ value cited is for a temperature of 25°C, we can use Equation 16.2.16: p$K_a$ + p$K_b$ = p$K_w$ = 14.00. Substituting the p$K_a$ and solving for the p$K_b$,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

   Because p$K_b$ = −log $K_b$, $K_b$ is $10^{-9.17} = 6.8 \times 10^{-10}$.

2. In this case, we are given $K_b$ for a base (dimethylamine) and asked to calculate $K_a$ and p$K_a$ for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is $K_b$ rather than p$K_b$, we can use Equation 16.23: $K_aK_b = K_w$. Substituting the values of $K_b$ and $K_w$ at 25°C and solving for $K_a$,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

   Because p$K_a$ = −log $K_a$, we have p$K_a$ = −log$(1.9 \times 10^{-11})$ = 10.72. We could also have converted $K_b$ to p$K_b$ to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

   If we are given any one of these four quantities for an acid or a base ($K_a$, p$K_a$, $K_b$, or p$K_b$), we can calculate the other three.

Exercise

Lactic acid [$CH_3CH(OH)CO_2H$] is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its p$K_a$ is 3.86 at 25°C. Calculate $K_a$ for lactic acid and p$K_b$ and $K_b$ for the lactate ion.

**Answer:** $K_a = 1.4 \times 10^{-4}$ for lactic acid; p$K_b$ = 10.14 and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

## Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 16.2.1 that acids like $H_2SO_4$ and $HNO_3$ lie *above* the hydronium ion, meaning that they have p$K_a$ values less than zero and are stronger acids than the $H_3O^+$ ion.Recall from Chapter 8 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving $HNO_3$ instead. In fact, all six of the common strong acids that we first encountered in Chapter 8 have p$K_a$ values less than zero, which means that they have a greater tendency to lose a proton than does the $H_3O^+$ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibriums for these strong acids lie far to the right, and

adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the $H_3O^+$ ion and the conjugate base of the acid.

Although $K_a$ for HI is about $10^8$ greater than $K_a$ for $HNO_3$, the reaction of either HI or $HNO_3$ with water gives an essentially stoichiometric solution of $H_3O^+$ and $I^-$ or $NO_3^-$. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M $H_3O^+$, *regardless of the identity of the strong acid*. This phenomenon is called the leveling effectThe phenomenon that makes $H_3O^+$ the strongest acid that can exist in water. Any species that is a stronger acid than $H_3O^+$ is leveled to the strength of $H_3O^+$ in aqueous solution.: any species that is a stronger acid than the conjugate acid of water ($H_3O^+$) is leveled to the strength of $H_3O^+$ in aqueous solution because $H_3O^+$ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and $HNO_3$ in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than $H_2O$. Measurements of the conductivity of 0.1 M solutions of both HI and $HNO_3$ in acetic acid show that HI is completely dissociated, but $HNO_3$ is only partially dissociated and behaves like a weak acid *in this solvent*. This result clearly tells us that HI is a stronger acid than $HNO_3$. The relative order of acid strengths and approximate $K_a$ and p$K_a$ values for the strong acids at the top of Table 16.2.1 were determined using measurements like this and different nonaqueous solvents.

### Note the Pattern

In aqueous solutions, [$H_3O^+$] is the strongest acid and $OH^-$ is the strongest base that can exist in equilibrium with $H_2O$.

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than $OH^-$ is leveled to the strength of $OH^-$ because $OH^-$ is the strongest base that can exist in equilibrium with water. Salts such as $K_2O$, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 16.3, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of $OH^-$ and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{16.2.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{16.2.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{16.2.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium ($CH_3Li$).

## Polyprotic Acids and Bases

As you learned in Chapter 8 , *polyprotic acids* such as $H_2SO_4$, $H_3PO_4$, and $H_2CO_3$ contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the p$K_a$ increases. Consider $H_2SO_4$, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with $H_2SO_4$ being a strong acid. In contrast, in the second reaction, appreciable quantities of both $HSO_4^-$ and $SO_4^{2-}$ are present at equilibrium.

### Note the Pattern

For a polyprotic acid, acid strength decreases and the p$K_a$ increases with the sequential loss of each proton.

The hydrogen sulfate ion ($HSO_4^-$) is both the conjugate base of $H_2SO_4$ and the conjugate acid of $SO_4^{2-}$. Just like water, $HSO_4^-$ can therefore act as *either* an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion ($SO_4^{2-}$) is a *polyprotic base* that is capable of accepting two protons in a stepwise manner:

$$SO_{4(aq)}^{2-} + H_2O_{(aq)} \rightleftharpoons HSO_{4(aq)}^{-} + OH_{(aq)}^{-}$$

$$HSO_{4(aq)}^{-} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH_{(aq)}^{-}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by $pK_a + pK_b = pK_w$. Consider, for example, the $HSO_4^-$/ $SO_4^{2-}$ conjugate acid–base pair. From Table 16.2.1, we see that the $pK_a$ of $HSO_4^-$ is 1.99. Hence the $pK_b$ of $SO_4^{2-}$ is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas $OH^-$ is a strong base, so the equilibrium shown above lies to the left. The $HSO_4^-$ ion is also a very weak base [$pK_a$ of $H_2SO_4$ = 2.0, $pK_b$ of $HSO_4^-$ = 14 − (−2.0) = 16], which is consistent with what we expect for the conjugate base of a strong acid. Thus the equilibrium also lies almost completely to the left. Once again, equilibrium favors the formation of the weaker acid–base pair.

## Example 16.2.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH_{4(aq)}^{+} + PO_{4(aq)}^{3-} \rightleftharpoons NH_{3(aq)} + HPO_{4(aq)}^{2-}$
- $CH_3CH_2CO_2H_{(aq)} + CN_{(aq)}^{-} \rightleftharpoons CH_3CH_2CO_{2(aq)}^{-} + HCN_{(aq)}$

**Given:** balanced chemical equation

**Asked for:** equilibrium position

**Strategy:**

Identify the conjugate acid–base pairs in each reaction. Then refer to Table 16.2.1 Table 16.2.2, and Figure 16.2.1 to determine which is the stronger acid and base. Equilibrium always favors the formation of the weaker acid–base pair.

**Solution:**

1. The conjugate acid–base pairs are $NH_4^+$/$NH_3$ and $HPO_4^{2-}$/$PO_4^{3-}$. According to Table 16.2 and Table 16.3, $NH_4^+$ is a stronger acid ($pK_a$ = 9.25) than $HPO_4^{2-}$ ($pK_a$ = 12.32), and $PO_4^{3-}$ is a stronger base ($pK_b$ = 1.68) than $NH_3$ ($pK_b$ = 4.75). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH_{4(aq)}^{+}} + \underset{\text{stronger base}}{PO_{4(aq)}^{3-}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO_{4(aq)}^{2-}}$$

2. The conjugate acid–base pairs are $CH_3CH_2CO_2H$/$CH_3CH_2CO_2^-$ and HCN/$CN^-$. According to Table 16.2.1, HCN is a weak acid ($pK_a$ = 9.21) and $CN^-$ is a moderately weak base ($pK_b$ = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 16.2.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties *are* listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid (−$CH_2CH_3$ versus −$CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the $pK_a$ of propionic acid to be similar in magnitude to the $pK_a$ of acetic acid. (In fact, the $pK_a$ of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN_{(aq)}^{-}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO_{2(aq)}^{-}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise

Predict whether the equilibrium for each reaction lies to the left or the right as written.

1. $H_2O_{(l)} + HS_{(aq)}^{-} \rightleftharpoons OH_{(aq)}^{-} + H_2S_{(aq)}$
2. $HCO_{2(aq)}^{-} + HSO_{4(aq)}^{-} \rightleftharpoons HCO_2H_{(aq)} + SO_{4(aq)}^{2-}$

**Answer**

1. left

2. left

## Acid–Base Properties of Solutions of Salts

We can also use the relative strengths of conjugate acid–base pairs to understand the acid–base properties of solutions of salts. In Chapter 8, you learned that a *neutralization reaction* can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as $Na^+$, replaces the proton on the acid. An example is the reaction of $CH_3CO_2H$, a weak acid, with NaOH, a strong base:

$$\underset{acid}{CH_3CO_2H_{(l)}} + \underset{base}{NaOH_{(s)}} \xrightarrow{H_2O} \underset{salt}{H_2OCH_3CO_2Na_{(aq)}} + \underset{water}{H_2O_{(l)}} \tag{16.2.22}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as NaCl dissolves in water, it produces $Na^+$(aq) and $Cl^-$(aq) ions. Using a Lewis approach, the $Na^+$ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The $Cl^-$ ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving NaCl in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations ($K^+$ and $Na^+$) have essentially no acidic character, but the anions ($CN^-$ and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)} \tag{16.2.23}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)} \tag{16.2.24}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table 16.2.2 and Figure 16.2.1, we can see that $CN^-$ is a stronger base ($pK_b$ = 4.79) than acetate ($pK_b$ = 9.24), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Figure 16.2.1). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

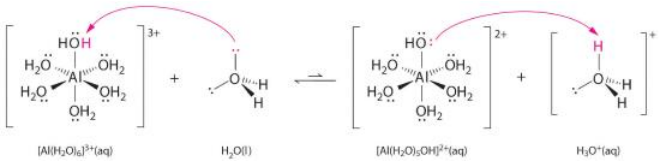
$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{16.2.25}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{16.2.26}$$

Figure 16.2.1 shows that $H_3O^+$ is a stronger acid than either $NH_4^+$ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The $H_3O^+$ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2.1, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation *and* the anion can react separately with water to produce an acid and a base, respectively? According to Eq 16.2.25, the ammonium ion will lower the pH, while according to Eq 16.2.24, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base ($pK_a \approx pK_b$). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the cation is a stronger acid than the anion is a base, the final solution has a pH < 7.00. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a pH > 7.00.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce $H_3O^+$. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure 16.2.2), as discussed in Chapter 8 . A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.



Second, the positive charge on the $Al^{3+}$ ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the O–H bonds, as shown in part (b) in Figure 16.2.2. With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free $H_2O$ molecule, making it easier to lose a $H^+$ ion.

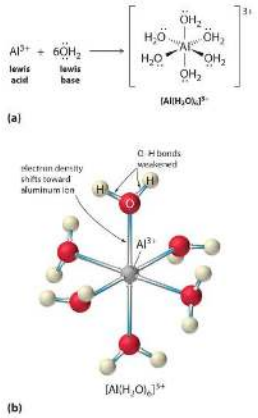


Figure 16.2.2 Effect of a Metal Ion on the Acidity of Water(a) Reaction of the metal ion $Al^{3+}$ with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

The magnitude of this effect depends on the following two factors (Figure 16.2.3):

1. **The *charge* on the metal ion.** A divalent ion ($M^{2+}$) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion ($M^+$) of the same radius.
2. **The *radius* of the metal ion.** For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

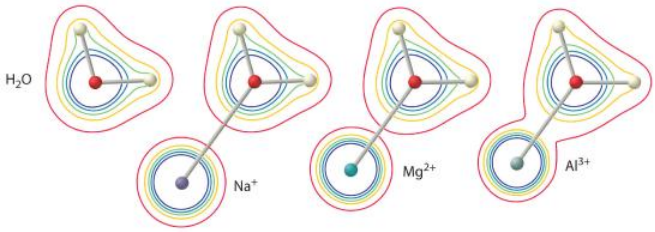


Figure 16.2.3 The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to $Na^+$, $Mg^{2+}$, and $Al^{3+}$ ions. These contour maps demonstrate that the smallest, most highly charged metal ion ($Al^{3+}$) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as $Al^{3+}$ and $Fe^{3+}$, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{16.2.27}$$

The $[Al(H_2O)_6]^{3+}$ ion has a p$K_a$ of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the *charge-to-radius ratio* of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as $Li^+$ and $Mg^{2+}$ or $Ca^{2+}$ and $Y^{3+}$, have different sizes and charges but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

### Note the Pattern

Solutions of small, highly charged metal ions in water are acidic.

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactionsA chemical reaction in which a salt reacts with water to yield an acidic or a basic solution.. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

### Note the Pattern

A hydrolysis reaction is an acid–base reaction.

### Example 16.2.3

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

1. $KNO_3$
2. $CrBr_3{\cdot}6H_2O$
3. $Na_2SO_4$

**Given:** compound

**Asked for:** acidity or basicity of aqueous solution

**Strategy:**

**A** Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.

**B** If the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

**Solution:**

1. **A** The $K^+$ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.

   **B** The $NO_3^-$ anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce $H^+$ or $OH^-$, and the solution will be neutral.

2. **A** The $Cr^{3+}$ ion is a relatively highly charged metal cation that should behave similarly to the $Al^{3+}$ ion and form the $[Cr(H_2O)_6]^{3+}$ complex, which will behave as a weak acid:

   $$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_(aq)$$

   **B** The $Br^-$ anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

3. **A** The $Na^+$ ion, like the $K^+$, is a very weak acid, so it should not affect the acidity of the solution.

**B** In contrast, $SO_4^{2-}$ is the conjugate base of $HSO_4^-$, which is a weak acid. Hence the $SO_4^{2-}$ ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

Exercise

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

1. KI
2. $Mg(ClO_4)_2$
3. NaHS

**Answer**

1. neutral
2. acidic
3. basic (due to the reaction of $HS^-$ with water to form $H_2S$ and $OH^-$)

## Summary

Two species that differ by only a proton constitute a **conjugate acid–base pair**. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the **acid ionization constant ($K_a$)**. Similarly, the equilibrium constant for the reaction of a weak base with water is the **base ionization constant ($K_b$)**. For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of p$K_a$ correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of p$K_b$ correspond to larger base ionization constants and hence stronger bases. At 25°C, p$K_a$ + p$K_b$ = 14.00. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than $H_3O^+$ and no base stronger than $OH^-$ can exist in aqueous solution, leading to the phenomenon known as the **leveling effect**. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base. A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion ($A^-$), the conjugate acid of a weak base as the cation ($BH^+$), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a **hydrolysis reaction**.

## Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

## Key Equations

**Acid ionization constant**

Equation 16.2.13: $K_a = K[H_2O] = \dfrac{[H_3O^+][A^-]}{[HA]}$

**Base ionization constant**

Equation 16.2.15: $K_b = K[H_2O] = [BH^+][OH^-][B]$

**Relationship between $K_a$ and $K_b$ of a conjugate acid–base pair**

Equation 16.2.20: $K_aK_b = K_w$

**Definition of p$K_a$**

Equation 16.2.21: $pKa = -\log_{10} K_a$

Equation 16.2.22: $K_a = 10^{-pK_a}$

**Definition of p$K_b$**

Equation 16.2.23: $pK_b = -\log_{10} K_b$

Equation 16.2.25: $K_b = 10^{-pK_b}$

**Relationship between p$K_a$ and p$K_b$ of a conjugate acid–base pair**

Equation 16.2.25: $pK_a + pK_b = pK_w$

Equation 16.29: $pK_a + pK_b = 14.00 \text{ at } 25°C$

## Conceptual Problems

1. Identify the conjugate acid–base pairs in each equilibrium.
    1. $HSO^-_{4(aq)} + H_2O_{(l)} \rightleftharpoons SO^{2-}_{4(aq)} + H_3O^+_{(aq)}$
    2. $C_3H_7NO_{2(aq)} + H_3O^+_{(aq)} \rightleftharpoons C_3H_8NO^+_{2(aq)} + H_2O_{(l)}$
    3. $CH_3CO_2H_{(aq)} + NH_{3(aq)} \rightleftharpoons CH_3CO^-_{2(aq)} + NH^+_{4(aq)}$
    4. $SbF_{5(aq)} + 2HF_{(aq)} \rightleftharpoons H_2F^+_{(aq)} + SbF^-_{6(aq)}$
2. Identify the conjugate acid–base pairs in each equilibrium.
    1. $HF(aq) + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$
    2. $CH_3CH_2NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2NH^+_{3(aq)} + OH^-_{(aq)}$
    3. $C_3H_7NO_{2(aq)} + OH^-_{(aq)} \rightleftharpoons C_3H_6NO^-_{2(aq)} + H_2O_{(l)}$
    4. $CH_3CO_2H_{(aq)} + 2HF_{(aq)} \rightleftharpoons CH_3C(OH)_2 + (aq) + HF^-_{2(aq)}$
3. Salts such as NaH contain the hydride ion ($H^-$). When sodium hydride is added to water, it produces hydrogen gas in a highly vigorous reaction. Write a balanced chemical equation for this reaction and identify the conjugate acid–base pairs.
4. Write the expression for $K_a$ for each reaction.
    1. $HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)}$
    2. $formic\ acid_{(aq)} + H_2O_{(l)} \rightleftharpoons formate_{(aq)} + H_3O^+_{(aq)}$
    3. $H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4(aq)} + H_3O^+_{(aq)}$
5. Write an expression for the ionization constant $K_b$ for each reaction.
    1. $OCH^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons HOCH_{3(aq)} + OH - (aq)$
    2. $NH^-_{2(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + OH^-_{(aq)}$
    3. $S^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-_{(aq)} + OH^-_{(aq)}$
6. Predict whether each equilibrium lies primarily to the left or to the right.
    1. $HBr_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Br^-_{(aq)}$
    2. $NaH_{(soln)} + NH_{3(l)} \rightleftharpoons H2(soln) + NaNH_{2(soln)}$
    3. $OCH^-_{3(aq)} + NH_{3(aq)} \rightleftharpoons CH3OH(aq) + NH^-_{2(aq)}$
    4. $NH_{3(aq)} + HCl_{(aq)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$
7. Species that are strong bases in water, such as $CH_3^-$, $NH_2^-$, and $S^{2-}$, are leveled to the strength of $OH^-$, the conjugate base of $H_2O$. Because their relative base strengths are indistinguishable in water, suggest a method for identifying which is the strongest base. How would you distinguish between the strength of the acids $HIO_3$, $H_2SO_4$, and $HClO_4$?
8. Is it accurate to say that a 2.0 M solution of $H_2SO_4$, which contains two acidic protons per molecule, is 4.0 M in $H^+$? Explain your answer.
9. The alkalinity of soil is defined by the following equation: alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$. The source of both $HCO_3^-$ and $CO_3^{2-}$ is $H_2CO_3$. Explain why the basicity of soil is defined in this way.
10. Why are aqueous solutions of salts such as $CaCl_2$ neutral? Why is an aqueous solution of $NaNH_2$ basic?
11. Predict whether aqueous solutions of the following are acidic, basic, or neutral.
    1. $Li_3N$
    2. NaH
    3. KBr
    4. $C_2H_5NH_3^+Cl^-$
12. When each compound is added to water, would you expect the pH of the solution to increase, decrease, or remain the same?

1. $LiCH_3$
2. $MgCl_2$
3. $K_2O$
4. $(CH_3)_2NH_2^+Br^-$

13. Which complex ion would you expect to be more acidic—$Pb(H_2O)_4^{2+}$ or $Sn(H_2O)_4^{2+}$? Why?
14. Would you expect $Sn(H_2O)_4^{2+}$ or $Sn(H_2O)_6^{4+}$ to be more acidic? Why?
15. Is it possible to arrange the hydrides LiH, RbH, KH, CsH, and NaH in order of increasing base strength in aqueous solution? Why or why not?

## Answer

1. 1. $\underset{\text{base 2}}{\overset{\text{acid 1}}{HSO^-_{4(aq)}}} + H_2O_{(l)} \rightleftharpoons \underset{\text{acid 2}}{\overset{\text{base 1}}{SO^{2-}_{4(aq)}}} + H_3O^+_{(aq)}$
   2. $\underset{\text{base 2}}{C_3H_7NO_{2(aq)}} + \overset{\text{acid 1}}{H_3O^+_{(aq)}} \rightleftharpoons \underset{\text{acid 2}}{C_3H_8NO^+_{2(aq)}} + \overset{\text{base 1}}{H_2O_{(l)}}$
   3. $\overset{\text{acid 1}}{HOAc_{(aq)}} + \underset{\text{base 2}}{NH_{3(aq)}} \rightleftharpoons \overset{\text{base 1}}{CH_3CO^-_{2(aq)}} + \underset{\text{acid 2}}{NH^+_{4(aq)}}$
   4. $\overset{\text{acid 1}}{SbF_{5(aq)}} + \underset{\text{base 2}}{2HF_{(aq)}} \rightleftharpoons \underset{\text{acid 2}}{H_2F^+_{(aq)}} + \overset{\text{base 1}}{SbF^-_6(aq)}$
2. 
3. 
4. 
5. 
6. 
7. 
8. 
9. 
10. 
11. 
12. 
13. 
14. 
15. 

## Numerical Problems

1. Arrange these acids in order of increasing strength.
   - acid A: p$K_a$ = 1.52
   - acid B: p$K_a$ = 6.93
   - acid C: p$K_a$ = 3.86

   Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?
2. Arrange these bases in order of increasing strength:
   - base A: p$K_b$ = 13.10
   - base B: p$K_b$ = 8.74
   - base C: p$K_b$ = 11.87

   Given solutions with the same initial concentration of each base, which would have the highest percent ionization?
3. Calculate the $K_a$ and the p$K_a$ of the conjugate acid of a base with each p$K_b$ value.
   1. 3.80
   2. 7.90

3. 13.70
4. 1.40
5. −2.50

4. Benzoic acid is a food preservative with a p$K_a$ of 4.20. Determine the $K_b$ and the p$K_b$ for the benzoate ion.
5. Determine $K_a$ and p$K_a$ of boric acid [$B(OH)_3$], solutions of which are occasionally used as an eyewash; the p$K_b$ of its conjugate base is 4.80.

## Answers

1. acid B < acid C < acid A (strongest)
2. 
3. 1. $K_a = 6.3 \times 10^{-11}$; p$K_a$ = 10.20
   2. $K_a = 7.9 \times 10^{-7}$; p$K_a$ = 6.10
   3. $K_a$ = 0.50; p$K_a$ = 0.30
   4. $K_a = 2.5 \times 10^{-13}$; p$K_a$ = 12.60
   5. $K_a = 3.2 \times 10^{-17}$; p$K_a$ = 16.50
4. 
5. $K_a = 6.3 \times 10^{-10}$ p$K_a$ = 9.20

## Contributors

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Modified by Joshua B. Halpern

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# 16.3: Molecular Structure and Acid-Base Strength

**Learning Objectives**

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

## Bond Strengths

In general, the stronger the A–H or B–$H^+$ bond, the less likely the bond is to break to form $H^+$ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

| Relative Acid Strength | HF | < | HCl | < | HBr | < | HI |
|---|---|---|---|---|---|---|---|
| H–X Bond Energy (kJ/mol) | 570 | | 432 | | 366 | | 298 |
| p$K_a$ | 3.20 | | −6.1 | | −8.9 | | −9.3 |

The trend in bond energies is due to a steady decrease in overlap between the 1*s* orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, *acid strengths of binary hydrides increase as we go down a column of the periodic table*. For example, the order of acidity for the binary hydrides of Group 16 is as follows, with p$K_a$ values in parentheses: $H_2O$ (14.00 = p$K_w$) < $H_2S$ (7.05) < $H_2Se$ (3.89) < $H_2Te$ (2.6).

## Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$ the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or $BH^+$). *Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H+ and makes the parent acid a stronger acid.* Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with p$K_a$ values in parentheses: $CH_4$ (~50) << $NH_3$ (~36) < $H_2O$ (14.00) < HF (3.20).

Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of $CH_4$ is $CH_3^-$, and the conjugate base of HF is $F^-$. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the $F^-$ ion than carbon can stabilize the negative charge in the $CH_3^-$ ion. Consequently, HF has a greater tendency to dissociate to form $H^+$ and $F^-$ than does methane to form $H^+$ and $CH_3^-$, making HF a much stronger acid than $CH_4$.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form $E^-$ and $H^+$. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, *acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table*.

### Note the Pattern

Acid strengths of binary hydrides *increase* as we go *down* a column or *from left to right* across a row of the periodic table.

## Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an *inductive effect*, and, much like the coordination of water to a metal ion, it can have a major

effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{16.3.1}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

| HOX | Electronegativity of X | p$K_a$ |
|---|---|---|
| HOCl | 3.0 | 7.40 |
| HOBr | 2.8 | 8.55 |
| HOI | 2.5 | 10.5 |

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as $H^+$.

The acidity of oxoacids, with the general formula $HOXO_n$ ($n$ = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 16.3.1, the $K_a$ values of the oxoacids of chlorine increase by a factor of about $10^4$ to $10^6$ with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

### Note the Pattern

Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 16.3.1 show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 16.3.1 and Figure 16.3.2, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from HClO to $HClO_4$ (also written as $HOClO_3$), while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as $H^+$ ions, thereby increasing the strength of the acid.

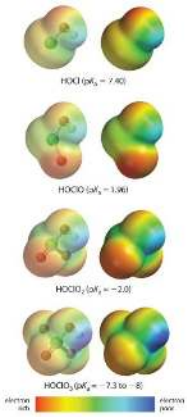


Figure 16.3.1 The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities.

Source: Chlorine oxoacids p$K_a$ values from J. R. Bowser, *Inorganic Chemistry* (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 16.3.2 , the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal

oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms. The electrostatic potential plots in Figure 16.3.2 demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in $ClO^-$ is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in $ClO_4^-$, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion ($ClO_4^-$), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion ($OCl^-$), the negative charge is largely localized on a single oxygen atom (Figure 16.3.2). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.

## Note the Pattern

Electron delocalization in the conjugate base increases acid strength.

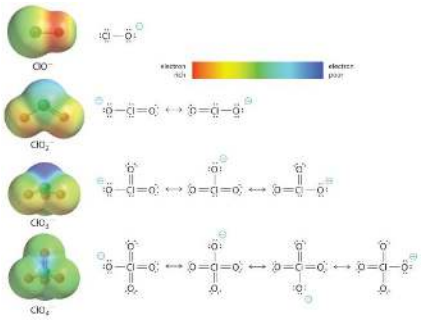


Figure 16.3.2 The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, $H_3PO_4$ is a weak acid, $H_2SO_4$ is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.

Careful inspection of the data in Table 16.3.1 shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid ($H_2CO_3$) were a discrete molecule with the structure $(HO)_2C{=}O$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid ($H_3PO_4$), for which $pK_{a1} = 2.16$. Instead, the tabulated value of $pK_{a1}$ for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see in Section 16.6, however, $H_2CO_3$ is only a minor component of the aqueous solutions of $CO_2$ that are referred to as carbonic acid. Similarly, if phosphorous acid ($H_3PO_3$) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as HOCl ($pK_a = 7.40$). In fact, the $pK_{a1}$ for phosphorous acid is 1.30, and the structure of phosphorous acid is $(HO)_2P(=O)H$ with one H atom directly bonded to P and one P=O bond. Thus the $pK_{a1}$ for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as $H_3PO_4$. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

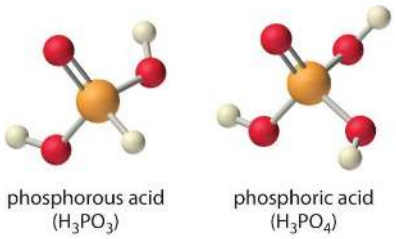


**Table 16.3.1 Values of p$K_a$ for Selected Polyprotic Acids and Bases**

| Polyprotic Acids | Formula | p $K_{a1}$ | p $K_{a2}$ | p $K_{a3}$ |
|---|---|---|---|---|
| carbonic acid* | "$H_2CO_3$" | 6.35 | 10.33 | |
| citric acid | $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$ | 3.13 | 4.76 | 6.40 |
| malonic acid | $HO_2CCH_2CO_2H$ | 2.85 | 5.70 | |
| oxalic acid | $HO_2CCO_2H$ | 1.25 | 3.81 | |
| phosphoric acid | $H_3PO_4$ | 2.16 | 7.21 | 12.32 |
| phosphorous acid | $H_3PO_3$ | 1.3 | 6.70 | |
| succinic acid | $HO_2CCH_2CH_2CO_2H$ | 4.21 | 5.64 | |
| sulfuric acid | $H_2SO_4$ | −2.0 | 1.99 | |
| sulfurous acid* | "$H_2SO_3$" | 1.85 | 7.21 | |
| | | | | |
| **Polyprotic Bases** | **Formula** | p $K_{b1}$ | p $K_{b2}$ | |
| ethylenediamine | $H_2N(CH_2)_2NH_2$ | 4.08 | 7.14 | |
| piperazine | $HN(CH_2CH_2)_2NH$ | 4.27 | 8.67 | |
| propylenediamine | $H_2N(CH_2)_3NH_2$ | 3.45 | 5.12 | |

*$H_2CO_3$ and $H_2SO_3$ are at best minor components of aqueous solutions of $CO_2$(g) and $SO_2$(g), respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the p$K_a$ values for several acetic acid derivatives:

$$pK_a CH_3CO_2H 4.76 < CH_2ClCO_2H 2.87 < CHCl_2CO_2H 1.35 < CCl_3CO_2H 0.66 < CF_3CO_2H 0.52$$

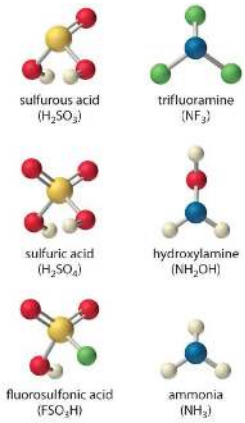
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $–CH_3$ group of acetic acid by a $–CF_3$ group results in about a 10,000-fold increase in acidity!

### Example 16.3.1

Arrange the compounds of each series in order of increasing acid or base strength.

1. sulfuric acid [$H_2SO_4$, or $(HO)_2SO_2$], fluorosulfonic acid ($FSO_3H$, or $FSO_2OH$), and sulfurous acid [$H_2SO_3$, or $(HO)_2SO$]
2. ammonia ($NH_3$), trifluoramine ($NF_3$), and hydroxylamine ($NH_2OH$)

The structures are shown here.




**Given:** series of compounds

**Asked for:** relative acid or base strengths

**Strategy:**

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

**Solution:**

1. Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove *more* electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, $FSO_3H$ is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured p$K_a$ values for these acids:

$$pKaH_2SO_31.85 < H_2SO_4^{-2} < FSO_3H - 10$$

2. The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in $NH_3$ are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an $H^+$ ion. Thus $NF_3$ is predicted to be a much weaker base than $NH_3$. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in $NH_3$ by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured p$K_b$ values:

$$pK_bNF_3— << NH_2OH8.06 < NH_34.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has not been measured.

Exercise

Arrange the compounds of each series in order of

1. decreasing acid strength: $H_3PO_4$, $CH_3PO_3H_2$, and $HClO_3$.
2. increasing base strength: $CH_3S^-$, $OH^-$, and $CF_3S^-$.

**Answer**

1. $HClO_3 > CH_3PO_3H_2 > H_3PO_4$
2. $CF_3S^- < CH_3S^- < OH^-$

## Summary

The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–$H^+$ bond, the more likely it is to dissociate to form an $H^+$ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of $H^+$, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an *inductive effect*, which can weaken an O–H bond and allow hydrogen to be more easily lost as $H^+$ ions.

## Key Takeaway

- Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound.

## Conceptual Problems

1. Section 16.3 presented several factors that affect the relative strengths of acids and bases. For each pair, identify the most important factor in determining which is the stronger acid or base in aqueous solution.
    1. $CH_3CCl_2CH_2CO_2H$ versus $CH_3CH_2CH_2CO_2H$
    2. $CH_3CO_2H$ versus $CH_3CH_2OH$
    3. HClO versus HBrO
    4. $CH_3C(=O)NH_2$ versus $CH_3CH_2NH_2$
    5. $H_3AsO_4$ versus $H_3AsO_3$
2. The stability of the conjugate base is an important factor in determining the strength of an acid. Which would you expect to be the stronger acid in aqueous solution—$C_6H_5NH_3^+$ or $NH_4^+$? Justify your reasoning.
3. Explain why $H_2Se$ is a weaker acid than HBr.
4. Arrange the following in order of decreasing acid strength in aqueous solution: $H_3PO_4$, $CH_3PO_3H_2$, and $HClO_3$.
5. Arrange the following in order of increasing base strength in aqueous solution: $CH_3S^-$, $OH^-$, and $CF_3S^-$.
6. Arrange the following in order of increasing acid strength in aqueous solution: $HClO_2$, $HNO_2$, and $HNO_3$.
7. Do you expect $H_2SO_3$ or $H_2SeO_3$ to be the stronger acid? Why?
8. Give a plausible explanation for why $CF_3OH$ is a stronger acid than $CH_3OH$ in aqueous solution. Do you expect $CHCl_2CH_2OH$ to be a stronger or a weaker acid than $CH_3OH$? Why?
9. Do you expect $Cl_2NH$ or $NH_3$ to be the stronger base in aqueous solution? Why?

## Answers

1.
2.
3.
4.
5. $CF_3S^- < CH_3S^- < OH^-$ (strongest base)
6.
7.
8.
9. $NH_3$; Cl atoms withdraw electron density from N in $Cl_2NH$.

## Contributors

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Modified by Joshua B. Halpern

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# 16.4: Quantitative Aspects of Acid-Base Equilibria

**Learning Objectives**

- To use $K_a$ and $K_b$ values to calculate the percent ionization and the pH of a solution of an acid or a base.

This section presents a quantitative approach to analyzing acid–base equilibriums. You will learn how to determine the values of $K_a$ and $K_b$, how to use $K_a$ or $K_b$ to calculate the percent ionization and the pH of an aqueous solution of an acid or a base, and how to calculate the equilibrium constant for the reaction of an acid with a base from the $K_a$ and $K_b$ of the reactants.

## Determining $K_a$ and $K_b$

The ionization constants $K_a$ and $K_b$ are equilibrium constants that are calculated from experimentally measured concentrations, just like the equilibrium constants discussed in Chapter 15. Before proceeding further, it is important to understand exactly what is meant when we describe the concentration of an aqueous solution of a weak acid or a weak base. Suppose, for example, we have a bottle labeled 1.0 M acetic acid or 1.0 M ammonia. As you learned in Chapter 8, such a solution is usually prepared by dissolving 1.0 mol of acetic acid or ammonia in water and adding enough water to give a final volume of exactly 1.0 L. If, however, we were to list the actual concentrations of all the species present in either solution, we would find that *none* of the values is exactly 1.0 M because a weak acid such as acetic acid or a weak base such as ammonia always reacts with water to some extent. The extent of the reaction depends on the $K_a$ or the $K_b$, the concentration of the acid or the base, and the temperature. Consequently, only the *total concentration* of both the ionized and unionized species is equal to 1.0 M.

The *analytical concentration* ($C$) is defined as the *total* concentration of all forms of an acid or a base that are present in solution, regardless of their state of protonation. Thus a "1.0 M" solution of acetic acid has an analytical concentration of 1.0 M, which is the sum of the *actual* concentrations of unionized acetic acid ($CH_3CO_2H$) and the ionized form ($CH_3CO_2^-$):

$$C_{CH_3CO_2H} = [CH_3CO_2H] + [CH_3CO_2^-] \tag{16.4.1}$$

As we shall see shortly, if we know the analytical concentration and the $K_a$, we can calculate the actual values of $[CH_3CO_2H]$ and $[CH_3CO_2^-]$.

The equilibrium equations for the reaction of acetic acid and ammonia with water are as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \tag{16.4.2}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{16.4.3}$$

where $K_a$ and $K_b$ are the ionization constants for acetic acid and ammonia, respectively. In addition to the analytical concentration of the acid (or the base), we must have a way to measure the concentration of at least *one* of the species in the equilibrium constant expression to determine the $K_a$ (or the $K_b$). There are two common ways to obtain the concentrations: (1) measure the electrical conductivity of the solution, which is related to the total concentration of ions present, and (2) measure the pH of the solution, which gives $[H^+]$ or $[OH^-]$.

Example 6 and Example 7 illustrate the procedure for determining $K_a$ for a weak acid and $K_b$ for a weak base. In both cases, we will follow the procedure developed in Chapter 15: the analytical concentration of the acid or the base is the *initial* concentration, and the stoichiometry of the reaction with water determines the *change* in concentrations. The *final* concentrations of all species are calculated from the initial concentrations and the changes in the concentrations. Inserting the final concentrations into the equilibrium constant expression enables us to calculate the $K_a$ or the $K_b$.

### Example 16.4.1

Electrical conductivity measurements indicate that 0.42% of the acetic acid molecules in a 1.00 M solution are ionized at 25°C. Calculate $K_a$ and $pK_a$ for acetic acid at this temperature.

**Given:** analytical concentration and percent ionization

**Asked for:** $K_a$ and p$K_a$

**Strategy:**

**A** Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

**B** Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

**C** Substitute the final concentrations into the equilibrium constant expression and calculate the $K_a$. Take the negative logarithm of $K_a$ to obtain the p$K_a$.

**Solution:**

**A** The balanced equilibrium equation for the dissociation of acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH3CO^-_{2(aq)} \tag{16.4.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \tag{16.4.2}$$

**B** To calculate the $K_a$, we need to know the equilibrium concentrations of $CH_3CO_2H$, $CH_3CO_2^-$, and $H^+$. The most direct way to do this is to construct a table that lists the initial concentrations and the changes in concentrations that occur during the reaction to give the final concentrations, using the procedure introduced in Chapter 15. The initial concentration of unionized acetic acid ($[CH_3CO_2H]_i$) is the analytical concentration, 1.00 M, and the initial acetate concentration ($[CH_3CO_2^-]_i$) is zero. The initial concentration of $H^+$ is not zero, however; $[H^+]_i$ is $1.00 \times 10^{-7}$ M due to the autoionization of water. The measured percent ionization tells us that 0.42% of the acetic acid molecules are ionized at equilibrium. Consequently, the change in the concentration of acetic acid is $\Delta[CH_3CO_2H] = -(4.2 \times 10^{-3})(1.00\ M) = -0.0042$ M. Conversely, the change in the acetate concentration is $\Delta[CH_3CO_2^-] = +0.0042$ M because every 1 mol of acetic acid that ionizes gives 1 mol of acetate. Because one proton is produced for each acetate ion formed, $\Delta[H^+] = +0.0042$ M as well. These results are summarized in the following table.

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO^-_{2(aq)} \tag{16.4.3}$$

| | $[CH_3CO_2H]$ | $[H^+]$ | $[CH_3CO_2^-]$ |
|---|---|---|---|
| initial | 1.00 | $1.00 \times 10^{-7}$ | 0 |
| change | −0.0042 | +0.0042 | +0.0042 |
| final | | | |

The final concentrations of all species are therefore as follows:

- $[CH_3CO_2H]_f = [CH_3CO_2H]_i + \Delta[CH_3CO_2H] = 1.00\ M + (-0.0042\ M) = 1.00\ M$
- $[CH_3CO_2^-]_f = [CH_3CO_2^-]_i + \Delta[CH_3CO_2^-] = 0\ M + (+0.0042\ M) = 0.0042\ M$
- $[H^+]_f = [H^+]_i + \Delta[H^+] = 1.00 \times 10^{-7} M + (+0.0042\ M) = 0.0042\ M$

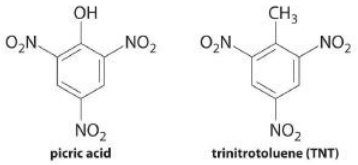
**C** We can now calculate $K_a$ by inserting the final concentrations into the equilibrium constant expression:

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.0042)(0.0042)}{1.00} = 1.8 \times 10^{-5} \tag{16.4.4}$$

The p$K_a$ is the negative logarithm of $K_a$: $pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$.

Exercise

Picric acid is the common name for 2,4,6-trinitrophenol, a derivative of phenol ($C_6H_5OH$) in which three H atoms are replaced by nitro ($–NO_2$) groups. The presence of the nitro groups removes electron density from the phenyl ring, making picric acid a much stronger acid than phenol ($pK_a$ = 9.99). The nitro groups also make picric acid potentially explosive, as you might expect based on its chemical similarity to 2,4,6-trinitrotoluene, better known as TNT. A 0.20 M solution of picric acid is 73% ionized at 25°C. Calculate $K_a$ and $pK_a$ for picric acid.




**Answer:** $K_a$ = 0.39; $pK_a$ = 0.41

### Example 16.4.2

A 1.0 M aqueous solution of ammonia has a pH of 11.63 at 25°C. Calculate $K_b$ and $pK_b$ for ammonia.

**Given:** analytical concentration and pH

**Asked for:** $K_b$ and $pK_b$

**Strategy:**

**A** Write the balanced equilibrium equation for the reaction and derive the equilibrium constant expression.

**B** Use the data given and the stoichiometry of the reaction to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations for all species in the equilibrium constant expression.

**C** Substitute the final concentrations into the equilibrium constant expression and calculate the $K_b$. Take the negative logarithm of $K_b$ to obtain the $pK_b$.

**Solution:**

**A** The balanced equilibrium equation for the reaction of ammonia with water is as follows:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

and the equilibrium constant expression is as follows:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Remember that water does not appear in the equilibrium constant expression for $K_b$.

**B** To calculate $K_b$, we need to know the equilibrium concentrations of $NH_3$, $NH_4^+$, and $OH^-$. The initial concentration of $NH_3$ is the analytical concentration, 1.0 M, and the initial concentrations of $NH_4^+$ and $OH^-$ are 0 M and $1.00 \times 10^{-7}$ M, respectively. In this case, we are given the pH of the solution, which allows us to calculate the final concentration of one species ($OH^-$) directly, rather than the change in concentration. Recall that $pK_w$ = pH + pOH = 14.00 at 25°C. Thus pOH = 14.00 − pH = 14.00 − 11.63 = 2.37, and $[OH^-]_f = 10^{-2.37} = 4.3 \times 10^{-3}$ M. Our data thus far are listed in the following table.

$$NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{16.4.5}$$

| | $[NH_3]$ | $[NH_4^+]$ | $[OH^-]$ |
|---|---|---|---|
| initial | 1.0 | 0 | $1.00 \times 10^{-7}$ |
| change | | | |
| final | | | $4.3 \times 10^{-3}$ |

The final [$OH^-$] is much greater than the initial [$H^+$], so the change in [$OH^-$] is as follows:

$\Delta[OH^-] = (4.3 \times 10^{-3}\ M) - (1.00 \times 10^{-7}\ M) \approx 4.3 \times 10^{-3}\ M$

The stoichiometry of the reaction tells us that 1 mol of $NH_3$ is converted to $NH_4^+$ for each 1 mol of $OH^-$ formed, so

$\Delta[NH_4^+] = +4.3 \times 10^{-3}\ M$ and $\Delta[NH_3] = -4.3 \times 10^{-3}\ M$

We can now insert these values for the changes in concentrations into the table, which enables us to complete the table.

$$H_2O_{(l)} + NH3_{(aq)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^- \tag{16.4.6}$$

| | [$NH_3$] | [$NH_4^+$] | [$OH^-$] |
|---|---|---|---|
| initial | 1.0 | 0 | $1.00 \times 10^{-7}$ |
| change | $-4.3 \times 10^{-3}$ | $+4.3 \times 10^{-3}$ | $+4.3 \times 10^{-3}$ |
| final | 1.0 | $4.3 \times 10^{-3}$ | $4.3 \times 10^{-3}$ |

**C** Inserting the final concentrations into the equilibrium constant expression gives $K_b$:

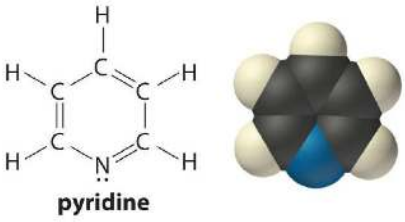
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(4.3 \times 10^{-3})^2}{1.0} = 1.8 \times 10^{-5}$$

and $pK_b = -\log K_b = 4.74$.

The $K_b$ and the $pK_b$ for ammonia are almost exactly the same as the $K_a$ and the $pK_a$ for acetic acid at 25°C. In other words, ammonia is almost exactly as strong a base as acetic acid is an acid. Consequently, the extent of the ionization reaction in an aqueous solution of ammonia at a given concentration is the same as in an aqueous solution of acetic acid at the same concentration.

Exercise

The pH of a 0.050 M solution of pyridine ($C_6H_5N$) is 8.96 at 25°C. Calculate $K_b$ and $pK_b$ for pyridine.



pyridine

**Answer:** $K_b = 1.7 \times 10^{-9}$; $pK_b = 8.77$

## Calculating Percent Ionization from $K_a$ or $K_b$

When carrying out a laboratory analysis, chemists frequently need to know the concentrations of all species in solution. Because the reactivity of a weak acid or a weak base is usually very different from the reactivity of its conjugate base or acid, we often need to know the percent ionization of a solution of an acid or a base to understand a chemical reaction. The percent ionization is defined as follows:

$$\text{percent ionization of acid} = \frac{[H^+]}{C_{HA}} \times 100 \tag{16.4.4}$$

$$\text{percent ionization of base} = \frac{[OH^-]}{C_B} \times 100 \tag{16.4.5}$$

One way to determine the concentrations of species in solutions of weak acids and bases is a variation of the tabular method we used previously to determine $K_a$ and $K_b$ values. As a demonstration, we will calculate the concentrations of all species and the

percent ionization in a 0.150 M solution of formic acid at 25°C. The data in Table E1 show that formic acid ($K_a$ = 1.8 × $10^{-4}$ at 25°C) is a slightly stronger acid than acetic acid. The equilibrium equation for the ionization of formic acid in water is as follows:

$$HCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{2(aq)} \tag{16.4.6}$$

and the equilibrium constant expression for this reaction is as follows:

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} \tag{16.4.7}$$

We set the initial concentration of $HCO_2H$ equal to 0.150 M, and that of $HCO_2^-$ is 0 M. The initial concentration of $H^+$ is 1.00 × $10^{-7}$ M due to the autoionization of water. Because the equilibrium constant for the ionization reaction is small, the equilibrium will lie to the left, favoring the unionized form of the acid. Hence we can define *x* as the amount of formic acid that dissociates.

If the change in [$HCO_2H$] is −*x*, then the change in [$H^+$] and [$HCO_2^-$] is +*x*. The final concentration of each species is the sum of its initial concentration and the change in concentration, as summarized in the following table.

$$HCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{2(aq)} \tag{16.4.7}$$

| | [$HCO_2H$] | [$H^+$] | [$HCO_2^-$] |
|---|---|---|---|
| initial | 0.150 | 1.00 × $10^{-7}$ | 0 |
| change | −*x* | +*x* | +*x* |
| final | (0.150 − *x*) | (1.00 × $10^{-7}$ + *x*) | *x* |

We can calculate *x* by substituting the final concentrations from the table into the equilibrium constant expression:

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(1.00 \times 10^{-7} + x)x}{0.150 - x} \tag{16.4.8}$$

Because the ionization constant $K_a$ is small, *x* is likely to be small compared with the initial concentration of formic acid: (0.150 − *x*) M ≈ 0.150 M. Moreover, [$H^+$] due to the autoionization of water (1.00 × $10^{-7}$ M) is likely to be negligible compared with [$H^+$] due to the dissociation of formic acid: (1.00 × $10^{-7}$ + *x*) M ≈ *x* M. Inserting these values into the equilibrium constant expression and solving for *x*,

$$K_a = \frac{x^2}{0.150} = 1.8 \times 10^{-4} \tag{16.4.9}$$

$$x = 5.2 \times 10^{-3} \tag{16.4.10}$$

We can now calculate the concentrations of the species present in a 0.150 M formic acid solution by inserting this value of *x* into the expressions in the last line of the table:

$$[HCO_2H] = (0.150 - x)\ M = 0.145\ M \tag{16.4.11}$$

$$[HCO_2] = x = 5.2 \times 10^{-3}\ M \tag{16.4.12}$$

$$[H^+] = (1.00 \times 10 - 7 + x)M = 5.2 \times 10^{-3}M \tag{16.4.13}$$

Thus the pH of the solution is –log(5.2 × $10^{-3}$) = 2.28. We can also use these concentrations to calculate the fraction of the original acid that is ionized. In this case, the percent ionization is the ratio of [$H^+$] (or [$HCO_2^-$]) to the analytical concentration, multiplied by 100 to give a percentage:

$$\text{percent ionization} = \frac{[H^+]}{C_{HA}} \times 100 = \frac{5.2 \times 10^{-3}\ M}{0.150} \times 100 = 3.5\% \tag{16.4.14}$$

*Always check to make sure that any simplifying assumption was valid.* As a general rule of thumb, approximations such as those used here are valid *only* if the quantity being neglected is no more than about 5% of the quantity to which it is being added or from

which it is being subtracted. If the quantity that was neglected is much greater than about 5%, then the approximation is probably not valid, and you should go back and solve the problem using the quadratic formula. In the previous demonstration, both simplifying assumptions were justified: the percent ionization is only 3.5%, which is well below the approximately 5% limit, and the $1.00 \times 10^{-7}$ M $[H^+]$ due to the autoionization of water is much, much less than the $5.2 \times 10^{-3}$ M $[H^+]$ due to the ionization of formic acid.

As a general rule, the $[H^+]$ contribution due to the autoionization of water can be ignored as long as the product of the acid or the base ionization constant and the analytical concentration of the acid or the base is at least 10 times greater than the $[H^+]$ or $[OH^-]$ from the autoionization of water—that is, if

$$K_a C_{HA} \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6} \tag{16.4.8}$$

or

$$K_b C_B \geq 10(1.00 \times 10^{-7}) = 1.0 \times 10^{-6} \tag{16.4.9}$$

By substituting the appropriate values for the formic acid solution into Equation 16.45, we see that the simplifying assumption is valid in this case:

$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5} > 1.0 \times 10^{-6} \tag{16.4.10}$$

Doing this simple calculation before solving this type of problem saves time and allows you to write simplified expressions for the final concentrations of the species present. In practice, it is necessary to include the $[H^+]$ contribution due to the autoionization of water only for extremely dilute solutions of very weak acids or bases.

Example 8 illustrates how the procedure outlined previously can be used to calculate the pH of a solution of a weak base.

### Example 16.4.3

Calculate the pH and percent ionization of a 0.225 M solution of ethylamine ($CH_3CH_2NH_2$), which is used in the synthesis of some dyes and medicines. The p$K_b$ of ethylamine is 3.19 at 20°C.

**Given:** concentration and p$K_b$

**Asked for:** pH and percent ionization

**Strategy:**

**A** Write the balanced equilibrium equation for the reaction and the equilibrium constant expression. Calculate $K_b$ from p$K_b$.

**B** Use Equation 16.4.8 to see whether you can ignore $[H^+]$ due to the autoionization of water. Then use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[OH^-]$. Use Equation 16.4.5 to calculate the percent ionization.

**C** Use the relationship $K_w = [OH^-][H^+]$ to obtain $[H^+]$. Then calculate the pH of the solution.

**Solution:**

**A** We begin by writing the balanced equilibrium equation for the reaction:

$$CH_3CH_2NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CH_2NH^+_{3(aq)} + OH^-_{(aq)}$$

The corresponding equilibrium constant expression is as follows:

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2}]$$

From the $pK_b$, we have $K_b = 10 - 3.19 = 6.5 \times 10^{-4}$.

**B** To calculate the pH, we need to determine the $H^+$ concentration. Unfortunately, $H^+$ does not appear in either the chemical equation or the equilibrium constant expression. However, $[H^+]$ and $[OH^-]$ in an aqueous solution are related by $K_w = [H^+][OH^-]$. Hence if we can determine $[OH^-]$, we can calculate $[H^+]$ and then the pH. The initial concentration of $CH_3CH_2NH_2$ is 0.225 M, and the initial $[OH^-]$ is $1.00 \times 10^{-7}$ M. Because ethylamine is a weak base, the extent of the reaction will be small, and it makes

sense to let $x$ equal the amount of $CH_3CH_2NH_2$ that reacts with water. The change in $[CH_3CH_2NH_2]$ is therefore $-x$, and the change in both $[CH_3CH_2NH_3^+]$ and $[OH^-]$ is $+x$. To see whether the autoionization of water can safely be ignored, we substitute $K_b$ and $C_B$ into Equation 16.4.10:

$$K_bC_B = (6.5 \times 10^{-4})(0.225) = 1.5 \times 10^{-4} > 1.0 \times 10^{-6}$$

Thus the simplifying assumption is valid, and we will not include $[OH^-]$ due to the autoionization of water in our calculations.

$$H_2O_{(l)} + CH_3CH_2NH_{2(aq)} \rightleftharpoons CH_3CH_2NH^+_{3(aq)} + OH^-_{(aq)} \tag{16.4.15}$$

| | $[CH_3CH_2NH_2]$ | $[CH_3CH_2NH_3^+]$ | $[OH^-]$ |
|---|---|---|---|
| initial | 0.225 | 0 | $1.00 \times 10^{-7}$ |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.225 - x)$ | $x$ | $x$ |

Substituting the quantities from the last line of the table into the equilibrium constant expression,

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]} = \frac{(x)(x)}{0.225 - x} = 6.5 \times 10^{-4}$$

As before, we assume the amount of $CH_3CH_2NH_2$ that ionizes is small compared with the initial concentration, so $[CH_3CH_2NH_2]_f = 0.225 - x \approx 0.225$. With this assumption, we can simplify the equilibrium equation and solve for $x$:

$$K_b = \frac{x^2}{0.225} = 6.5 \times 10^{-4}$$

$$x = 0.012 = [CH_3CH_2NH_3^+]_f = [OH^-]_f$$

The percent ionization is therefore

$$\text{percent ionization} = \frac{[OH^-]}{C_B} \times 100 = \frac{0.012\ M}{0.225\ M} \times 100 = 5.4\% \tag{16.4.16}$$

which is at the upper limit of the approximately 5% range that can be ignored. The final hydroxide concentration is thus 0.012 M.

**C** We can now determine the $[H^+]$ using the expression for $K_w$:

$$K_w = [OH^-][H^+]$$

$$1.01 \times 10^{-14} = (0.012\ M)[H^+]$$

$$8.4 \times 10^{-13}\ M = [H^+]$$

The pH of the solution is $-\log(8.4 \times 10^{-13}) = 12.08$. Alternatively, we could have calculated pOH as $-\log(0.012) = 1.92$ and determined the pH as follows:

$$pH + pOH = pKw = 14.00$$

$$pH = 14.00 - 1.92 = 12.08$$

The two methods are equivalent.

Exercise

Aromatic amines, in which the nitrogen atom is bonded directly to a phenyl ring ($-C_6H_5$) tend to be much weaker bases than simple alkylamines. For example, aniline ($C_6H_5NH_2$) has a $pK_b$ of 9.13 at 25°C. What is the pH of a 0.050 M solution of aniline?

**Answer:** 8.78

The previous examples illustrate a key difference between solutions of strong acids and bases and solutions of weak acids and bases. Because strong acids and bases ionize essentially completely in water, the percent ionization is always approximately 100%,

regardless of the concentration. In contrast, the percent ionization in solutions of weak acids and bases is small and depends on the analytical concentration of the weak acid or base. As illustrated for benzoic acid in Figure 16.4.1, the percent ionization of a weak acid or a weak base actually *increases* as its analytical concentration decreases. The percent ionization also increases as the magnitude of $K_a$ and $K_b$ increases.

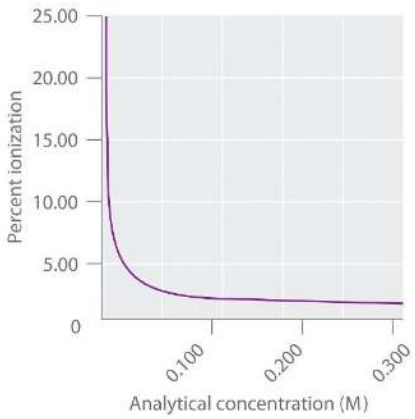



Figure 16.4.1 The Relationship between the Analytical Concentration of a Weak Acid and Percent **Ionization** As shown here for benzoic acid ($C_6H_5CO_2H$), the percent ionization decreases as the analytical concentration of a weak acid increases.

Unlike the $K_a$ or the $K_b$, the percent ionization is not a constant for weak acids and bases but depends on *both* the $K_a$ or the $K_b$ *and* the analytical concentration. Consequently, the procedure in Example 8 must be used to calculate the percent ionization and pH for solutions of weak acids and bases. Example 9 and its corresponding exercise demonstrate that the combination of a dilute solution and a relatively large $K_a$ or $K_b$ can give a percent ionization much greater than 5%, making it necessary to use the quadratic equation to determine the concentrations of species in solution.

### Note the Pattern

The percent ionization in a solution of a weak acid or a weak base *increases* as the analytical concentration *decreases* and as the $K_a$ or the $K_b$ *increases*.

### Example 16.4.4

Benzoic acid ($C_6H_5CO_2H$) is used in the food industry as a preservative and medically as an antifungal agent. Its p$K_a$ at 25°C is 4.20, making it a somewhat stronger acid than acetic acid. Calculate the percentage of benzoic acid molecules that are ionized in each solution.

1. a 0.0500 M solution
2. a 0.00500 M solution

**Given:** concentrations and p$K_a$

**Asked for:** percent ionization

**Strategy:**

**A** Write both the balanced equilibrium equation for the ionization reaction and the equilibrium equation (Equation 16.2.2). Use Equation 16.2.13 to calculate the $K_a$ from the p$K_a$.

**B** For both the concentrated solution and the dilute solution, use a tabular format to write expressions for the final concentrations of all species in solution. Substitute these values into the equilibrium equation and solve for $[C_6H_5CO_2^-]_f$ for each solution.

**C** Use the values of $[C_6H_5CO_2^-]_f$ and Equation 16.4.4 to calculate the percent ionization.

**Solution:**

**A** If we abbreviate benzoic acid as $PhCO_2H$ where Ph = $–C_6H_5$, the balanced equilibrium equation for the ionization reaction and the equilibrium equation can be written as follows:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)}$$

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]}$$

From the p$K_a$, we have $K_a = 10^{-4.20} = 6.3 \times 10^{-5}$.

1. **B** For the more concentrated solution, we set up our table of initial concentrations, changes in concentrations, and final concentrations:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)} \tag{16.4.17}$$

| | [$PhCO_2H$] | [$H^+$] | [$PhCO_2^-$] |
|---|---|---|---|
| initial | 0.0500 | $1.00 \times 10^{-7}$ | 0 |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.0500 - x)$ | $(1.00 \times 10^{-7} + x)$ | $x$ |

Inserting the expressions for the final concentrations into the equilibrium equation and making our usual assumptions, that [$PhCO_2^-$] and [$H^+$] are negligible due to the autoionization of water,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = \frac{(x)(x)}{0.0500 - x} = \frac{x^2}{0.0500} = 6.3 \times 10^{-5}$$

$$1.8 \times 10^{-3} = x$$

This value is less than 5% of 0.0500, so our simplifying assumption is justified, and [$PhCO_2^-$] at equilibrium is $1.8 \times 10^{-3}$ M. We reach the same conclusion using $C_{HA}$: $K_aC_{HA} = (6.3 \times 10^{-5})(0.0500) = 3.2 \times 10^{-6} > 1.0 \times 10^{-6}$.

**C** The percent ionized is the ratio of the concentration of $PhCO_2^-$ to the analytical concentration, multiplied by 100:

$$\text{percent ionized} = \frac{[PhCO_2^-]}{C_{PhCO_2H}} \times 100 = \frac{1.8 \times 10^{-30}}{0.0500} \times 100 = 3.6\%$$

Because only 3.6% of the benzoic acid molecules are ionized in a 0.0500 M solution, our simplifying assumptions are confirmed.

2. **B** For the more dilute solution, we proceed in exactly the same manner. Our table of concentrations is therefore as follows:

$$PhCO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + PhCO^-_{2(aq)} \tag{16.4.18}$$

| | [$PhCO_2H$] | [$H^+$] | [$PhCO_2^-$] |
|---|---|---|---|
| initial | 0.00500 | $1.00 \times 10^{-7}$ | 0 |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.00500 - x)$ | $(1.00 \times 10^{-7} + x)$ | $x$ |

Inserting the expressions for the final concentrations into the equilibrium equation and making our usual simplifying assumptions,

$$K_a = \frac{[H^+][PhCO_2^-]}{[PhCO_2H]} = \frac{(x)(x)}{0.00500 - x} = \frac{x^2}{0.00500} = 6.3 \times 10^{-5}$$

$$5.6 \times 10^{-4} = x$$

Unfortunately, this number is greater than 10% of 0.00500, so our assumption that the fraction of benzoic acid that is ionized in this solution could be neglected and that $(0.00500 - x) \approx x$ is not valid. Furthermore, we see that $K_aC_{HA} = (6.3 \times 10^{-5})(0.00500) = 3.2 \times 10^{-7} < 1.0 \times 10^{-6}$. Thus the relevant equation is as follows:

$$\frac{x^2}{0.00500 - x} = 6.3 \times 10^{-5}$$

which must be solved using the quadratic formula. Multiplying out the quantities,

$x^2 = (6.3 \times 10^{-5})(0.00500 - x) = (3.2 \times 10^{-7}) - (6.3 \times 10^{-5})x$

Rearranging the equation to fit the standard quadratic equation format,

$x^2 + (6.3 \times 10^{-5})x - (3.2 \times 10^{-7}) = 0$

This equation can be solved by using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(6.3 \times 10^{-5}) \pm \sqrt{(6.3 \times 10^{-5})^2 - 4(1)(-3.2 \times 10^{-7})}}{2(1)}$$

$$x = \frac{-(6.3 \times 10^{-5}) \pm (1.1 \times 10^{-3})}{2} = 5.3 \times 10^{-4}$$

or

$$x = -5.9 \times 10^{-4}$$

Because a negative $x$ value corresponds to a negative [$PhCO_2^-$], which is not physically meaningful, we use the positive solution: $x = 5.3 \times 10^{-4}$. Thus [$PhCO_2^-$] = $5.3 \times 10^{-4}$ M.

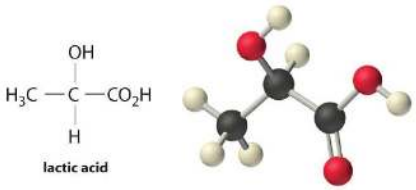
**C** The percent ionized is therefore

$$\text{percent ionized} = \frac{[PhCO_2^-]C_{PhCO_2H}}{\times} 100 = \frac{5.3 \times 10^{-4}}{0.00500} \times 100 = 11\%$$

In the more dilute solution ($C$ = 0.00500 M), 11% of the benzoic acid molecules are ionized versus only 3.6% in the more concentrated solution ($C$ = 0.0500 M). Decreasing the analytical concentration by a factor of 10 results in an approximately threefold increase in the percentage of benzoic acid molecules that are ionized.

Exercise

Lactic acid ($CH_3CH(OH)CO_2H$) is a weak acid with a p$K_a$ of 3.86 at 25°C. What percentage of the lactic acid is ionized in each solution?




1. a 0.10 M solution
2. a 0.0020 M solution

**Answer**

1. 3.7%
2. 23%

## Determining $K_{eq}$ from $K_a$ and $K_b$

In Section 16.2 , you learned how to use $K_a$ and $K_b$ values to qualitatively predict whether reactants or products are favored in an acid–base reaction. Tabulated values of $K_a$ (or p$K_a$) and $K_b$ (or p$K_b$), plus the $K_w$, enable us to quantitatively determine the direction

and extent of reaction for a weak acid and a weak base by calculating $K$ for the reaction. To illustrate how to do this, we begin by writing the dissociation equilibriums for a weak acid and a weak base and then summing them:

$$acid: \quad HA \rightleftharpoons H^+ + A^- \quad K_a \tag{16.4.11a}$$

$$base: \quad B + H_2O \rightleftharpoons HB^+ + OH^- \quad K_b \tag{16.4.11b}$$

$$sum: \quad HA + B + H_2O \rightleftharpoons H^+ + A^- + HB^+ + OH^- \quad K_{sum} = K_aK_b \tag{16.4.11c}$$

The overall reaction has $H_2O$ on the left and $H^+$ and $OH^-$ on the right, which means it involves the autoionization of water ($H_2O \rightleftharpoons H^+ + OH^-$) in addition to the acid–base equilibrium in which we are interested. We can obtain an equation that includes only the acid–base equilibrium by simply adding the equation for the reverse of the autoionization of water ($H^+ + OH^- \rightleftharpoons H_2O$), for which $K = 1/K_w$, to the overall equilibrium in Equation 16.4.11 and canceling:

$$HA + B + \cancel{H_2O} \rightleftharpoons \cancel{H^+} + A^- + HB^+ + \cancel{OH^-} \quad K_{sum} = K_aK_b \tag{16.4.12a}$$

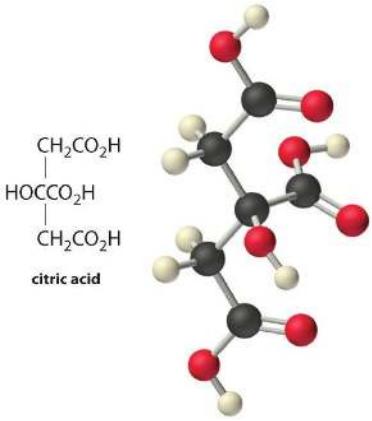
$$\cancel{H^+} + \cancel{OH^-} \rightleftharpoons \cancel{H_2O} \quad 1/K_w \tag{16.4.12b}$$

$$HA + B \rightleftharpoons A^- + HB^+ \quad K = (K_aK_b)/K_w \tag{16.4.12c}$$

Thus the equilibrium constant for the reaction of a weak acid with a weak base is the product of the ionization constants of the acid and the base divided by $K_w$. Example 10 illustrates how to calculate the equilibrium constant for the reaction of a weak acid with a weak base.

### Example 16.4.5

Fish tend to spoil rapidly, even when refrigerated. The cause of the resulting “fishy” odor is a mixture of amines, particularly methylamine ($CH_3NH_2$), a volatile weak base ($pK_b$ = 3.34). Fish is often served with a wedge of lemon because lemon juice contains citric acid, a triprotic acid with $pK_a$ values of 3.13, 4.76, and 6.40 that can neutralize amines. Calculate the equilibrium constant for the reaction of excess citric acid with methylamine, assuming that only the first dissociation constant of citric acid is important.




**Given:** $pK_b$ for base and $pK_a$ for acid

**Asked for:** $K$

**Strategy:**

**A** Write the balanced equilibrium equation and the equilibrium constant expression for the reaction.

**B** Convert $pK_a$ and $pK_b$ to $K_a$ and $K_b$ and then use Equation 16.4.12 to calculate $K$.

**Solution:**

**A** If we abbreviate citric acid as $H_3$citrate, the equilibrium equation for its reaction with methylamine is as follows:

$$CH_3NH_{2(aq)} + H_3citrate_{(aq)} \rightleftharpoons CH_3NH^+_{3(aq)} + H_2citrate^-_{(aq)}$$

The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CH_3NH_3^+][H_2citrate^-]}{[CH_3NH_2][H_3citrate]}$$

**B** Equation 16.49 is $K = (K_aK_b)/K_w$. Converting p$K_a$ and p$K_b$ to $K_a$ and $K_b$ gives $K_a = 10^{-3.13} = 7.4 \times 10^{-4}$ for citric acid and $K_b = 10^{-3.34} = 4.6 \times 10^{-4}$ for methylamine. Substituting these values into the equilibrium equation,

$$K = \frac{K_aK_b}{K_w} = \frac{(7.4 \times 10^{-4})(4.6 \times 10^{-4})}{1.01 \times 10^{-14}} = 3.4 \times 10^7$$

The value of p$K$ can also be calculated directly by taking the negative logarithm of both sides of Equation 16.49, which gives

\(pK = pK_a + pK_b − pK_w = 3.13 + 3.34 − 14.00 = −7.53 \notag \]

Thus $K = 10^{-(-7.53)} = 3.4 \times 10^7$, in agreement with the earlier value. In either case, the $K$ values show that the reaction of citric acid with the volatile, foul-smelling methylamine lies very far to the right, favoring the formation of a much less volatile salt with no odor. This is one reason a little lemon juice helps make less-than-fresh fish more appetizing.

Exercise

Dilute aqueous ammonia solution, often used as a cleaning agent, is also effective as a deodorizing agent. To see why, calculate the equilibrium constant for the reaction of aqueous ammonia with butyric acid ($CH_3CH_2CH_2CO_2H$), a particularly foul-smelling substance associated with the odor of rancid butter and smelly socks. The p$K_b$ of ammonia is 4.75, and the p$K_a$ of butyric acid is 4.83.

**Answer:** $2.6 \times 10^4$

## Summary

If the concentration of one or more of the species in a solution of an acid or a base is determined experimentally, $K_a$ and $K_b$ can be calculated, and $K_a$, p$K_a$, $K_b$, and p$K_b$ can be used to quantitatively describe the composition of solutions of acids and bases. The concentrations of all species present in solution can be determined, as can the pH of the solution and the percentage of the acid or base that is ionized. The equilibrium constant for the reaction of a weak acid with a weak base can be calculated from $K_a$ (or p$K_a$), $K_b$ (or p$K_b$), and $K_w$.

## Key Takeaway

- For a solution of a weak acid or a weak base, the percent ionization increases as the $K_a$ or the $K_b$ increases and as the analytical concentration decreases.

## Key Equations

**Percent ionization of acid**

Equation 16.4.4: $= \frac{[H^+]}{C_{HA}} \times 100$

**Percent ionization of base**

Equation 16.4.5: $= \frac{[OH^-]}{C_B} \times 100$

**Equilibrium constant for reaction of a weak acid with a weak base**

Equation 16.4.12: $K = \frac{K_aK_b}{K_w}$

## Conceptual Problems

1. Explain why the analytical concentration ($C$) of $H_2SO_4$ is equal to $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$.
2. Write an expression for the analytical concentration ($C$) of $H_3PO_4$ in terms of the concentrations of the species actually present in solution.

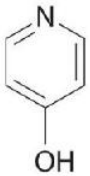
3. For relatively dilute solutions of a weak acid such as acetic acid ($CH_3CO_2H$), the concentration of undissociated acetic acid in solution is often assumed to be the same as the analytical concentration. Explain why this is a valid practice.
4. How does dilution affect the percent ionization of a weak acid or a weak base?
5. What is the relationship between the $K_a$ of a weak acid and its percent ionization? Does a compound with a large p$K_a$ value have a higher or a lower percent ionization than a compound with a small p$K_a$ value (assuming the same analytical concentration in both cases)? Explain.
6. For a dilute solution of a weak acid (HA), show that the pH of the solution can be approximated using the following equation (where $C_{HA}$ is the analytical concentration of the weak acid):

$$pH = -\log \sqrt{K_a C_{HA}} \tag{16.4.19}$$

Under what conditions is this approximation valid?

## Numerical Problems

1. The p$K_a$ of $NH_3$ is estimated to be 35. Its conjugate base, the amide ion ($NH_2^-$), can be isolated as an alkali metal salt, such as sodium amide ($NaNH_2$). Calculate the pH of a solution prepared by adding 0.100 mol of sodium amide to 1.00 L of water. Does the pH differ appreciably from the pH of a NaOH solution of the same concentration? Why or why not?
2. Phenol is a topical anesthetic that has been used in throat lozenges to relieve sore throat pain. Describe in detail how you would prepare a 2.00 M solution of phenol ($C_6H_5OH$) in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of phenol with water? Use the information in Table E1 and Table E2 to calculate the pH of the phenol solution.
3. Describe in detail how you would prepare a 1.50 M solution of methylamine in water; then write equations to show all the species present in the solution. What is the equilibrium constant expression for the reaction of methylamine with water? Use the information in Table E1 and Table E2 to calculate the pH of the solution.
4. A 0.200 M solution of diethylamine, a substance used in insecticides and fungicides, is only 3.9% ionized at 25°C. Write an equation showing the equilibrium reaction and then calculate the p$K_b$ of diethylamine. What is the p$K_a$ of its conjugate acid, the diethylammonium ion? What is the equilibrium constant expression for the reaction of diethylammonium chloride with water?
5. A 1.00 M solution of fluoroacetic acid ($FCH_2CO_2H$) is 5% dissociated in water. What is the equilibrium constant expression for the dissociation reaction? Calculate the concentration of each species in solution and then calculate the p$K_a$ of $FCH_2CO_2H$.
6. The p$K_a$ of 3-chlorobutanoic acid ($CH_3CHClCH_2CO_2H$) is 4.05. What percentage is dissociated in a 1.0 M solution? Do you expect the p$K_a$ of butanoic acid to be greater than or less than the p$K_a$ of 3-chlorobutanoic acid? Why?
7. The p$K_a$ of the ethylammonium ion ($C_2H_5NH_3^+$) is 10.64. What percentage of ethylamine is ionized in a 1.00 M solution of ethylamine?
8. The p$K_a$ of $Cl_3CCO_2H$ is 0.64. What is the pH of a 0.580 M solution? What percentage of the $Cl_3CCO_2H$ is dissociated?
9. The pH of a 0.150 M solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is 2.70. What is the p$K_b$ of the conjugate base, aniline ($C_6H_5NH_2$)? Do you expect the p$K_b$ of $(CH_3)_2CHNH_2$ to be greater than or less than the p$K_b$ of $C_6H_5NH_2$? Why?
10. What is the pH of a 0.620 M solution of $CH_3NH_3^+Br^-$ if the p$K_b$ of $CH_3NH_2$ is 10.62?
11. The p$K_b$ of 4-hydroxypyridine is 10.80 at 25°C. What is the pH of a 0.0250 M solution?




12. The p$K_a$ values of formic acid and the methylammonium ion are 3.75 and 10.62, respectively. Calculate $K$ for the following reaction:

$$HCO^-_{2(aq)} + CH_3NH^+_{3(aq)} \rightleftharpoons HCO_2H_{(aq)} + CH_3NH_{2(aq)} \tag{16.4.20}$$

13. The p$K_a$ values of butanoic acid and the ammonium ion are 4.82 and 9.24, respectively. Calculate $K$ for the following reaction:

$$CH_3CH_2CH_2CO^-_{2(aq)} + NH^+_{4(aq)} \rightleftharpoons CH_3CH_2CH_2CO_2H_{(aq)} + NH_{3(aq)} \tag{16.4.21}$$

14. Use the information in Tables E1 and E2 to calculate the pH of a 0.0968 M solution of calcium formate.
15. Calculate the pH of a 0.24 M solution of sodium lactate. The p$K_a$ of lactic acid is 3.86.
16. Use the information in Tables E1 and E2 to determine the pH of a solution prepared by dissolving 750.0 mg of methylammonium chloride ($CH_3NH_3^+Cl^-$) in enough water to make 150.0 mL of solution.
17. Use the information in Tables E1 and E2 to determine the pH of a solution prepared by dissolving 855 mg of sodium nitrite ($NaNO_2$) in enough water to make 100.0 mL of solution.

## Answers

1.
2.
3.
4.
5.
6.
7.
8.
9. p$K_b$ = 9.43; $(CH_3)_2CHNH_2$ will be a stronger base and have a lower p$K_b$; aniline is a weaker base because the lone pair on the nitrogen atom can be delocalized on the aromatic ring.
10.
11.
12.
13. $3.8 \times 10^{-5}$
14.
15.
16.
17. 8.18

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 16.5: Acid-Base Titrations

**Learning Objectives**

- To calculate the pH at any point in an acid–base titration.

In Chapter 8, you learned that in an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the *titrant*) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the *unknown*). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curveA plot of the pH of the solution being titrated versus the amount of acid or base (of known concentration) added.. The shape of the curve provides important information about what is occurring in solution during the titration.

## Titrations of Strong Acids and Bases

Part (a) of Figure 16.5.1 shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in part (b) in Figure 16.5.1 . As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

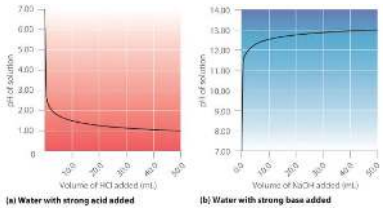



Figure 16.5.1 Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M NaOH.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of $H^+$ because of the neutralization reaction: $OH^- + H^+ \rightleftharpoons H_2O$ (in part (a) in Figure 16.5.2). Thus the pH of the solution increases gradually. Near the equivalence pointThe point in a titration where a stoichiometric amount of the titrant has been added., however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the $H^+$ ions originally present have been consumed. (For more information on titrations and the equivalence point, see Section 8.9 .) For the titration of a monoprotic strong acid (HCl) with a *monobasic* strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$\begin{aligned} moles\ of\ base &= (volume)_b(molarity)_b V_b M_b = moles\ of\ acid \\ &= (volume)_a(molarity)_a = V_a M_a \end{aligned} \tag{16.5.1}$$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for $V_b$:

$$V_b(0.20Me) = 0.025L = 25mL \tag{16.5.1}$$

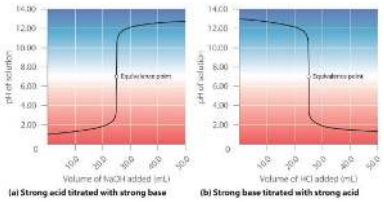



Figure 16.5.2 The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M NaOH, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more.

At the equivalence point (when 25.0 mL of NaOH solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more NaOH produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M NaOH.

As shown in part (b) in Figure 16.5.2, the titration of 50.0 mL of a 0.10 M solution of NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in part (a) in Figure 16.5.2. The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on *only* the concentrations of the acid and base, *not* their identities.

### Note the Pattern

The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

### Example 16.5.1

Calculate the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl.

**Given:** volumes and concentrations of strong base and acid

**Asked for:** pH

**Strategy:**

**A** Calculate the number of millimoles of $H^+$ and $OH^-$ to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.

**B** Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

**Solution:**

**A** Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of $H^+$ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00 \cancel{mL} \left( \frac{0.100\ mmol\ HCl}{\cancel{mL}} \right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90 \cancel{mL} \left( \frac{0.200\ mmol\ NaOH}{\cancel{mL}} \right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus $H^+$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $OH^-$ to the HCl solution. Because only 4.98 mmol of $OH^-$ has been added, the amount of excess $H^+$ is 5.00 mmol − 4.98 mmol = 0.02 mmol of $H^+$.

**B** The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $H^+$ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{=4}\ M$$

The pH is $-\log[H^+] = -\log(3 \times 10^{-4}) = 3.5$, which is significantly less than the pH of 7.00 for a neutral solution.

Exercise

Calculate the pH of a solution prepared by adding 40.00 mL of 0.237 M HCl to 75.00 mL of a 0.133 M solution of NaOH.

**Answer:** 11.6

## Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding $K_a$ or $K_b$. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned in Section 16.4, $[H^+]$ of a solution of a weak acid (HA) is *not* equal to the concentration of the acid but depends on both its $pK_a$ and its concentration. Because only a fraction of a weak acid dissociates, $[H^+]$ is less than [HA]. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration. Part (a) in Figure 16.5.3 shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M

HCl shown in part (a) in Figure 16.5.2 . Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the p$K_a$ of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

### Note the Pattern

The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the $K_a$ or $K_b$.

The titration curve in part (a) in Figure 16.5.3 was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of NaOH. The procedure is illustrated in the following subsection and Example 12 for three points on the titration curve, using the p$K_a$ of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$).

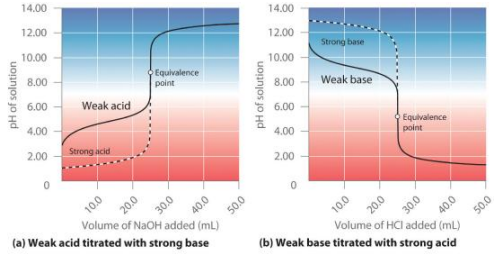



Figure 16.5.3 The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid(a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M $NH_3$, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line.

## Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained Section 16.4, if we know $K_a$ or $K_b$ and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a table of initial concentrations, changes in concentrations, and final concentrations. In this situation, the initial concentration of acetic acid is 0.100 M. If we define $x$ as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO_2^- \tag{16.5.2}$$

| | $[CH_3CO_2H]$ | $[H^+]$ | $[CH_3CO_2^-]$ |
|---|---|---|---|
| initial | 0.100 | $1.00 \times 10^{-7}$ | 0 |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.100 - x)$ | $x$ | $x$ |

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.4.8 and Equation 16.4.9 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100} = 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$

## Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M $CH_3CO_2H$ (part (a) in Figure 16.5.4). Because the neutralization reaction proceeds to completion, all of the $OH^-$ ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{16.5.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the *amounts* of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation (Equation 16.2.2) to determine [$H^+$] of the resulting solution.

**Step 1:** To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of $CH_3CO_2H$ in the original solution and the amount of $OH^-$ in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(CH_3CO_2H)/\cancel{mL}) = 5.00\ mmol(CH_3CO_2H)$$

The NaOH solution contained

5.00 mL=1.00 mmol (NaOH)

Comparing the amounts shows that $CH_3CO_2H$ is in excess. Because $OH^-$ reacts with $CH_3CO_2H$ in a 1:1 stoichiometry, the amount of excess $CH_3CO_2H$ is as follows:

5.00 mmol $CH_3CO_2H$ − 1.00 mmol $OH^-$ = 4.00 mmol $CH_3CO_2H$

Each 1 mmol of $OH^-$ reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following table, which shows the numbers of moles of the various species, *not* their concentrations.

$$CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO^-_2(aq) + H_2O(l) \tag{16.5.3}$$

| | [$CH_3CO_2H$] | [$OH^-$] | [$CH_3CO_2^-$] |
|---|---|---|---|
| **initial** | 5.00 mmol | 1.00 mmol | 0 mmol |
| **change** | −1.00 mmol | −1.00 mmol | +1.00 mmol |
| **final** | 4.00 mmol | 0 mmol | 1.00 mmol |

This table gives the initial amount of acetate and the final amount of $OH^-$ ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of $OH^-$ added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of $OH^-$, but the amount of $OH^-$ due to the autoionization of water is insignificant compared to the amount of $OH^-$ added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

**Step 2:** To calculate [$H^+$] at equilibrium following the addition of NaOH, we must first calculate [$CH_3CO_2H$] and [$CH_3CO_2^-$] using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and $K_a$ for acetic acid ($1.74 \times 10^{-5}$), we can use Equation 16.2.2 to calculate [$H^+$] at equilibrium:

$$K_a = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{(1.72 \times 10^{-5})\,(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

Calculating −log[$H^+$] gives pH = −log($6.95 \times 10^{-5}$) = 4.158.

Comparing the titration curves for HCl and acetic acid in part (a) in Figure 16.5.3, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to

4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example 16.5.2, we calculate another point for constructing the titration curve of acetic acid.

### Example 16.5.2

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

**Given:** volume and molarity of base and acid

**Asked for:** pH

**Strategy:**

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of $OH^-$ and $CH_3CO_2H$. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with $OH^-$, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate $K_b$ using the relationship $K_w = K_aK_b$ (Equation 16.2.10). Calculate $[OH^-]$ and use this to calculate the pH of the solution.

**Solution:**

**A** Ignoring the spectator ion ($Na^+$), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of $OH^-$ and $CH_3CO_2H$ are as follows:

$$25.00\ \cancel{mL}\left(\frac{0.200\ mmol\ OH^-}{\cancel{mL}}\right) = 5.00\ mmol\ OH^-$$

$$50.00\ \cancel{mL}\left(\frac{0.100\ mmol\ CH_3CO_2H}{\cancel{mL}}\right) = 5.00\ mmol\ CH_3CO_2H$$

The number of millimoles of $OH^-$ equals the number of millimoles of $CH_3CO_2H$, so neither species is present in excess.

**B** Because the number of millimoles of $OH^-$ added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

| $CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$ | | | |
|---|---|---|---|
| | $[CH_3CO_2H]$ | $[OH^-]$ | $[CH_3CO_2^-]$ |
| **initial** | 5.00 mmol | 5.00 mmol | 0 mmol |
| **final** | 0 mmol | 0 mmol | 5.00 mmol |
| **change** | −5.00 mmol | −5.00 mmol | +5.00 mmol |

**C** Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base *with water* to calculate $[H^+]$ at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[CH_3CO_2] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$CH_3CO_{2(aq)}^- + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction is $K_b = K_w/K_a$, where $K_a$ is the acid ionization constant of acetic acid. We therefore define $x$ as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

| $H_2O_{(l)} + CH_3CO^-_{2(aq)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$ | | | |
|---|---|---|---|
| | $[CH_3CO_2^-]$ | $[CH_3CO_2H]$ | $[OH^-]$ |
| **initial** | 0.0667 | 0 | $1.00 \times 10^{-7}$ |
| **change** | $-x$ | $+x$ | $+x$ |
| **final** | $(0.0667 - x)$ | $x$ | $x$ |

**D** Substituting the expressions for the final values from this table into Equation 16.2.5,

$$K_b = \frac{[CH_3CO_2H]\,[OH^-]}{[CH_3CO_2^-]} \approx= \frac{x \cdot x}{0.0667 - x} = \frac{x^2}{0.0667}$$

We can obtain $K_b$ by rearranging Equation 16.2.10 and substituting the known values:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} = \frac{x^2}{0.0667}$$

which we can solve to get $x = 6.22 \times 10^{-6}$. Thus $[OH^-] = 6.22 \times 10^{-6}$ M, and the pH of the final solution is 8.794 (part (a) in Figure 16.5.4). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce $OH^-$.

Exercise

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The $pK_b$ of ammonia is 4.75 at 25°C.

**Answer:** 9.23

As shown in part (b) in Figure 16.5.3, the titration curve for $NH_3$, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is *less* than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 16.5.4 illustrates the shape of titration curves as a function of the $pK_a$ or the $pK_b$. As the acid or the base being titrated becomes weaker (its $pK_a$ or $pK_b$ becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

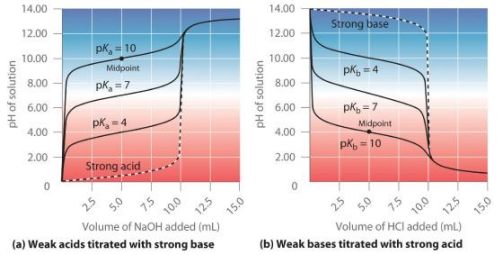



Figure 16.5.4 Effect of Acid or Base Strength on the Shape of Titration **Curves** Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the $pK_a$ or $pK_b$ of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated $pK_a$ values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated $pK_b$ values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to $pK_a = 10$ and $pK_b = 10$.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in part (a) in Figure 16.5.5 and part (b) in Figure 16.5.5 for the two shallowest curves. By definition, at the midpoint of the titration of an acid, $[HA] = [A^-]$. Recall from Equation 16.2.2 that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$log\ K_a = -log\,[H_3O^+]$$

From the definitions of p$K_a$ and pH, we see that this is identical to

$$pK_a = pH$$

Thus *the pH at the midpoint of the titration of a weak acid is equal to the p$K_a$ of the weak acid*, as indicated in part (a) in Figure 16.5.4 for the weakest acid where we see that the midpoint for p$K_a$ = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration *and* the p$K_a$ (or the p$K_b$) of a weak acid (or a weak base).

### Note the Pattern

The pH at the midpoint of the titration of a weak acid is equal to the p$K_a$ of the weak acid.

## Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the p$K_a$ values are separated by at least three p$K_a$ units, then the overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. A titration of the triprotic acid $H_3PO_4$ with NaOH is illustrated in Figure 16.5.5 and shows two well-defined steps: the first midpoint corresponds to p$K_{a1}$, and the second midpoint corresponds to p$K_{a2}$. Because $HPO_4^{2-}$ is such a weak acid, p$K_{a3}$ has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

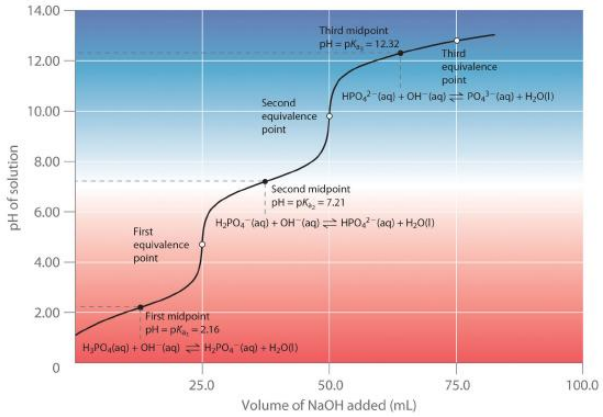
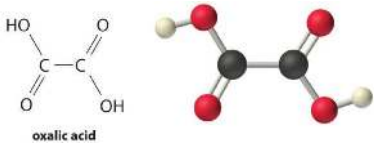



Figure 16.5.5 Titration Curve for Phosphoric Acid ($H_3PO_4$), a Typical Polyprotic **Acid**The curve for the titration of 25.0 mL of a 0.100 M $H_3PO_4$ solution with 0.100 M NaOH along with the species in solution at each $K_a$ is shown. Note the two distinct equivalence points corresponding to deprotonation of $H_3PO_4$ at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because $HPO_4^{2-}$ is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined.

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 16.5.5 The initial pH is high, but as acid is added, the pH decreases in steps if the successive p$K_b$ values are well separated. Table16.3.1 lists the ionization constants and p$K_a$ values for some common polyprotic acids and bases.

### Example 16.5.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid ($HO_2CCO_2H$), a diprotic acid (abbreviated as $H_2ox$). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($^-O_2CCO_2^-$, abbreviated $ox^{2-}$).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as $Ca^{2+}$ are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

**Given:** volume and concentration of acid and base

**Asked for:** pH

**Strategy:**

**A** Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.

**B** Calculate the concentrations of all the species in the final solution. Use Equation 16.2.3 to determine $[H^+]$ and convert this value to pH.

**Solution:**

**A** Table 16.3.1 gives the p$K_a$ values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00 \cancel{mL} \left( \frac{0.510\ mmol\ H_2ox}{\cancel{mL}} \right) = 5.10\ mmol\ H_2ox$$

$$55.00 \cancel{mL} \left( \frac{0.120\ mmol\ NaOH}{\cancel{mL}} \right) = 6.60\ mmol\ NaOH$$

The strongest acid ($H_2ox$) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of $OH^-$ to react with $Hox^-$, forming $ox^{2-}$ and $H_2O$. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

| | $H_2ox$ | $OH^-$ | $Hox^-$ | $ox^{2-}$ |
|---|---|---|---|---|
| initial | 5.10 mmol | 6.60 mmol | 0 mmol | 0 mmol |
| change (step 1) | −5.10 mmol | −5.10 mmol | +5.10 mmol | 0 mmol |
| final (step 1) | 0 mmol | 1.50 mmol | 5.10 mmol | 0 mmol |
| change (step 2) | — | −1.50 mmol | −1.50 mmol | +1.50 mmol |
| final | 0 mmol | 0 mmol | 3.60 mmol | 1.50 mmol |

**B** The equilibrium between the weak acid ($Hox^-$) and its conjugate base ($ox^{2-}$) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 12:

final volume of solution = 100.0 mL + 55.0 mL = 155.0 mL

Thus the concentrations of $Hox^-$ and $ox^{2-}$ are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate $[H^+]$ at equilibrium using the following equation:

$$K_{a2} == \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of $Hox^-$ and $ox^{2-}$,

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{[ox^{2-}]} = \frac{(1.6 \times 10^{-4})\,(2.32 \times 10^{-2})}{(9.68 \times 10^{-3})} = 3.7 \times 10^{-4}\ M$$

So

$$pH = -log\,[H^+] = -log\,(3.7 \times 10^{-4}) = 3.43$$

This answer makes chemical sense because the pH is between the first and second p$K_a$ values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than p$K_{a1}$), but we added only enough to titrate less than half of the second, less acidic proton, with p$K_{a2}$. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to p$K_{a2}$.

Exercise

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine ($pK_{b1}$ = 4.27, $pK_{b2}$ = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.




**Answer:** 4.9 (Video Solution)

## Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$HIn\,(aq) \rightleftharpoons H^+\,(aq) + In^-\,(aq)$$

where the protonated form is designated by HIn and the conjugate base by $In^-$. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[H^+]\,[In^-]}{HIn} \tag{16.5.4}$$

The $pK_{in}$ (its $pK_a$) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH (Figure 16.22). In all cases, though, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a $pK_{in}$ that is within one pH unit of the expected pH at the equivalence point of the titration.

**Figure 16.5.6 Naturally Oc** **ıtors in Red Cabbage Juice** Red cabbage juice contains a mixture of substances whose color depends on the pH. Each test ution of red cabbage juice in water, but the pH of the solutions varies from pH = 2.0 (far left) to pH = 11.0 (far right). At pH = blue. (From 99 Chemical on YouTube)

Synthetic indicators have be ıeet these criteria and cover virtually the entire pH range. Figure 16.5.7 shows the approximate pH range over which some change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

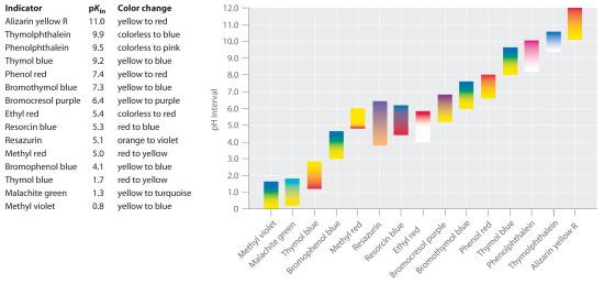



Figure 16.5.7 Some Common Acid–Base Indicators Approximate colors are shown, along with $pK_{in}$ values and the pH range over which the color changes.

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of $In^-$ increases, the color of the solution slowly changes from the characteristic color of HIn to that of $In^-$. As we will see in Section 16.6, the $[In^-]/[HIn]$ ratio changes from 0.1 at a pH one unit *below* $pK_{in}$ to 10 at a pH one unit *above* $pK_{in}$. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a p$K_{in}$ value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure 16.5.8. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M NaOH. The pH ranges over which two common indicators (methyl red, p$K_{in}$ = 5.0, and phenolphthalein, p$K_{in}$ = 9.5) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of NaOH has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the *midpoint* of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change color, resulting in a huge error.

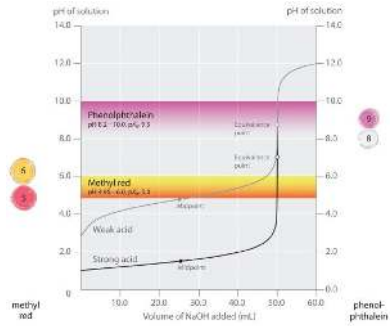



Figure 16.5.8 Choosing the Correct Indicator for an Acid–Base Titration The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M NaOH. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the p$K_{in}$ for methyl red (5.0) is very close to the p$K_a$ of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a p$K_{in}$ between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with p$K_{in}$ > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with p$K_{in}$ < 7.0, should be used.

The existence of many different indicators with different colors and p$K_{in}$ values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure 16.25).




Figure 16.5.9 pH Paper pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided.

## Summary

The shape of a **titration curve**, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The **equivalence point** of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases,

however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the **midpoint**, the point halfway on the titration curve to the equivalence point, is equal to the p$K_a$ of the weak acid or the p$K_b$ of the weak base. Thus titration methods can be used to determine both the concentration *and* the p$K_a$ (or the p$K_b$) of a weak acid (or a weak base). **Acid–base indicators** are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

### Key Takeaway

- Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the p$K_a$, and the p$K_b$ of the system.

### Conceptual Problems

1. Why is the portion of the titration curve that lies below the equivalence point of a solution of a weak acid displaced upward relative to the titration curve of a strong acid? How are the slopes of the curves different at the equivalence point? Why?
2. Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.
    1. An aqueous solution of NaOH is titrated with 0.100 M HCl.
    2. An aqueous solution of ethylamine ($CH_3CH_2NH_2$) is titrated with 0.150 M $HNO_3$
    3. An aqueous solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is titrated with 0.050 M KOH.
3. The p$K_a$ values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?
    1. titrating a solution of $Ba(OH)_2$ with 0.100 M HCl
    2. titrating a solution of trimethylamine ($Me_3N$) with 0.150 M $HNO_3$
    3. titrating a solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) with 0.050 M KOH
4. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not usually the case in titrations of weak acids or weak bases?
5. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?
6. Describe what is occurring on a molecular level during the titration of a weak acid, such as acetic acid, with a strong base, such as NaOH, at the following points along the titration curve. Which of these points corresponds to pH = p$K_a$?
    1. at the beginning of the titration
    2. at the midpoint of the titration
    3. at the equivalence point
    4. when excess titrant has been added
7. On a molecular level, describe what is happening during the titration of a weak base, such as ammonia, with a strong acid, such as HCl, at the following points along the titration curve. Which of these points corresponds to pOH = p$K_b$?
    1. at the beginning of the titration
    2. at the midpoint of the titration
    3. at the equivalence point
    4. when excess titrant has been added
8. For the titration of a weak acid with a strong base, use the $K_a$ expression to show that pH = p$K_a$ at the midpoint of the titration.
9. Chemical indicators can be used to monitor pH rapidly and inexpensively. Nevertheless, electronic methods are generally preferred. Why?
10. Why does adding ammonium chloride to a solution of ammonia in water decrease the pH of the solution?
11. Given the equilibrium system $CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$, explain what happens to the position of the equilibrium and the pH in each case.
    1. Dilute HCl is added.
    2. Dilute NaOH is added.
    3. Solid sodium acetate is added.
12. Given the equilibrium system $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$, explain what happens to the position of the equilibrium and the pH in each case.
    1. Dilute HCl is added.

2. Dilute NaOH is added.
3. Solid $CH_3NH_3^+Cl^-$ is added.

### Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. 1. shifts to left; pH decreases
    2. shifts to right; pH increases
    3. shifts to left; pH increases
12.

### Numerical Problems

1. Calculate the pH of each solution.
    1. A volume of 25.0 mL of 6.09 M HCl is added to 100.0 mL of distilled water
    2. A volume of 5.0 mL of 2.55 M NaOH is added to 75.0 mL of distilled water.
2. What is the pH of a solution prepared by mixing 50.0 mL of 0.225 M HCl with 100.0 mL of a 0.184 M solution of NaOH?
3. What volume of 0.50 M HCl is needed to completely neutralize 25.00 mL of 0.86 M NaOH?
4. Calculate the final pH when each pair of solutions is mixed.
    1. 100 mL of 0.105 M HCl and 100 mL of 0.115 M sodium acetate
    2. 50 mL of 0.10 M HCl and 100 mL of 0.15 M sodium acetate
    3. 100 mL of 0.109 M acetic acid and 100 mL of 0.118 M NaOH
    4. 100 mL of 0.998 M acetic acid and 50.0 mL of 0.110 M NaOH
5. Calculate the final pH when each pair of solutions is mixed.
    1. 100 mL of 0.983 M HCl and 100 mL of 0.102 M sodium fluoride
    2. 50.0 mL of 0.115 M HCl and 100 mL of 0.109 M sodium fluoride
    3. 100 mL of 0.106 M hydrofluoric acid and 50.0 mL of 0.996 M NaOH
    4. 100 mL of 0.107 M sodium acetate and 50.0 mL of 0.987 M acetic acid
6. Calcium carbonate is a major contributor to the “hardness” of water. The amount of $CaCO_3$ in a water sample can be determined by titrating the sample with an acid, such as HCl, which produces water and $CO_2$. Write a balanced chemical equation for this reaction. Generate a plot of solution pH versus volume of 0.100 M HCl added for the titration of a solution of 250 mg of $CaCO_3$ in 200.0 mL of water with 0.100 M HCl; assume that the HCl solution is added in 5.00 mL increments. What volume of HCl corresponds to the equivalence point?
7. For a titration of 50.0 mL of 0.288 M NaOH, you would like to prepare a 0.200 M HCl solution. The only HCl solution available to you, however, is 12.0 M.
    1. How would you prepare 500 mL of a 0.200 M HCl solution?
    2. Approximately what volume of your 0.200 M HCl solution is needed to neutralize the NaOH solution?
    3. After completing the titration, you find that your “0.200 M” HCl solution is actually 0.187 M. What was the exact volume of titrant used in the neutralization?
8. While titrating 50.0 mL of a 0.582 M solution of HCl with a solution labeled “0.500 M KOH,” you overshoot the endpoint. To correct the problem, you add 10.00 mL of the HCl solution to your flask and then carefully continue the titration. The total volume of titrant needed for neutralization is 71.9 mL.
    1. What is the actual molarity of your KOH solution?
    2. What volume of titrant was needed to neutralize 50.0 mL of the acid?

9. Complete the following table and generate a titration curve showing the pH versus volume of added base for the titration of 50.0 mL of 0.288 M HCl with 0.321 M NaOH. Clearly indicate the equivalence point.

| Base Added (mL) | 10.0 | 30.0 | 40.0 | 45.0 | 50.0 | 55.0 | 65.0 | 75.0 |
|---|---|---|---|---|---|---|---|---|
| pH | | | | | | | | |

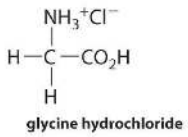
10. The following data were obtained while titrating 25.0 mL of 0.156 M NaOH with a solution labeled "0.202 M HCl." Plot the pH versus volume of titrant added. Then determine the equivalence point from your graph and calculate the exact concentration of your HCl solution.

| Volume of HCl (mL) | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
|---|---|---|---|---|---|---|---|
| pH | 11.46 | 11.29 | 10.98 | 4.40 | 2.99 | 2.70 | 2.52 |

11. Fill in the data for the titration of 50.0 mL of 0.241 M formic acid with 0.0982 M KOH. The p$K_a$ of formic acid is 3.75. What is the pH of the solution at the equivalence point?

| Volume of Base Added (mL) | 0 | 5 | 10 | 15 | 20 | 25 |
|---|---|---|---|---|---|---|
| pH | | | | | | |

12. Glycine hydrochloride, which contains the fully protonated form of the amino acid glycine, has the following structure:



glycine hydrochloride

It is a strong electrolyte that completely dissociates in water. Titration with base gives two equivalence points: the first corresponds to the deprotonation of the carboxylic acid group and the second to loss of the proton from the ammonium group. The corresponding equilibrium equations are as follows:

$$\begin{aligned} {}^{+}NH_3 - CH_2 - CO_2H\,(aq) &\rightleftharpoons \quad pK_{a1} = 2.3 \\ {}^{+}NH_3 - CH_2 - CO_2\,(aq) + H^+ & \qquad (16.5.4) \\ {}^{+}NH_3 - CH_2 - CO_2\,(aq) &\rightleftharpoons \quad pK_{a2} = 9.6 \\ NH_2 - CH_2 - COO\,(aq) + H^+ & \end{aligned}$$

1. Given 50.0 mL of solution that is 0.430 M glycine hydrochloride, how many milliliters of 0.150 M KOH are needed to fully deprotonate the carboxylic acid group?
2. How many additional milliliters of KOH are needed to deprotonate the ammonium group?
3. What is the pH of the solution at each equivalence point?
4. How many milliliters of titrant are needed to obtain a solution in which glycine has no net electrical charge? The pH at which a molecule such as glycine has no net charge is its *isoelectric point*. What is the isoelectric point of glycine?

13. What is the pH of a solution prepared by adding 38.2 mL of 0.197 M HCl to 150.0 mL of 0.242 M pyridine? The p$K_b$ of pyridine is 8.77.
14. What is the pH of a solution prepared by adding 40.3 mL of 0.289 M NaOH to 150.0 mL of 0.564 M succinic acid ($HO_2CCH_2CH_2CO_2H$)? (For succinic acid, p$K_{a1}$ = 4.21 and p$K_{a2}$ = 5.64).
15. Calculate the pH of a 0.15 M solution of malonic acid ($HO_2CCH_2CO_2H$), whose p$K_a$ values are as follows: p$K_{a1}$ = 2.85 and p$K_{a2}$ = 5.70.

## Answers

1.
2.
3. 43 mL
4. Video Solution

5. Video Solution
6. Video Solution
7. 1. dilute 8.33 mL of 12.0 M HCl to 500.0 mL
   2. 72 mL
   3. 77.0 mL
8. 
9. 
10. 
11. pH at equivalence point = 8.28

| Volume of Base Added (mL) | 0 | 5 | 10 | 15 | 20 | 25 |
|---|---|---|---|---|---|---|
| pH | 2.19 | 2.38 | 2.70 | 2.89 | 3.04 | 3.15 |

12. 
13. 
14. 
15. 1.85

## Contributors

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Modified by Joshua B. Halpern

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# 16.6: Buffers

**Learning Objectives**

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch equation to calculate the pH of a buffer.

BuffersSolutions that maintain a relatively constant pH when an acid or a base is added. are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base ($A^-$) or a weak base (B) and its conjugate acid ($BH^+$), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

## The Common Ion Effect

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of $H^+$). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution.

A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. Recall that the dissociation reaction of acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \leftrightharpoons CH_3CO^-_{(aq)} + H^+_{(aq)} \tag{16.6.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2]}{[CH_3CO_2H]} \tag{16.6.2}$$

Sodium acetate ($CH_3CO_2Na$) is a strong electrolyte that ionizes completely in aqueous solution to produce $Na^+$ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 16.6.1 will shift to the left, consuming some of the added $CH_3CO_2^-$ and some of the $H^+$ ions originally present in solution:

Because $Na^+$ is a spectator ion, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding *any* base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess $H^+$ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, *only the equilibrium composition has changed; the ionization constant $K_a$ for acetic acid remains the same*. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is called the common ion effectThe shift in equilibrium that results when a strong electrolyte containing one ion in common with a reaction system that is at equilibrium is added to the system..

### Note the Pattern

Adding a common ion to a system at equilibrium affects the equilibrium composition but not the ionization constant.

### Example 16.6.1

In Section 16.4, we calculated that a 0.150 M solution of formic acid at 25°C ($pK_a$ = 3.75) has a pH of 2.28 and is 3.5% ionized.

1. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
2. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

**Given:** solution concentration and pH, p$K_a$, and percent ionization of acid; final concentration of conjugate base or strong acid added

**Asked for:** pH and percent ionization of formic acid

**Strategy:**

**A** Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.

**B** Substitute the expressions for the final concentrations into the expression for $K_a$. Calculate [$H^+$] and the pH of the solution.

**C** Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

**Solution:**

1. **A** Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The $Na^+$ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H_{(aq)} \leftrightharpoons HCO^-_{2(aq)} + H^+_{(aq)}$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

$$HCO_2H_{(aq)} \leftrightharpoons HCO^-_{2(aq)} + H^+_{(aq)} \tag{16.6.1}$$

| | [$HCO_2H$] | [$H^+$] | [$HCO_2^-$] |
|---|---|---|---|
| initial | 0.150 | $1.00 \times 10^{-7}$ | 0.100 |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.150 - x)$ | $x$ | $(0.100 + x)$ |

**B** We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(x)\,(0.100 + x)}{0.150 + x} \approx \frac{x(0.100)}{0.150} = 10^{-3.75} = 1.8 \times 10^{-4}$$

Rearranging and solving for $x$,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} = 1.35 \times 10^{-4} = [HCO_2^-]$$

The value of $x$ is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover, $K_aC_{HA}$ = $(1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$, which is greater than $1.0 \times 10^{-6}$, so again, our assumption is justified. The final pH is $-\log(2.7 \times 10^{-4}) = 3.57$, compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of $H^+$ ions, driving the equilibrium to the left.

2. **C** Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H_{(aq)} \leftrightharpoons H^+_{(aq)} + HCO^-_{2(aq)} \tag{16.6.2}$$

| | [$HCO_2H$] | [$H^+$] | [$HCO_2^-$] |
|---|---|---|---|
| initial | 0.150 | 0.200 | 0 |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.150 - x)$ | $(0.200 + x)$ | $x$ |

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final [$HCO_2^-$]. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$Ka = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for $x$,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} = 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding $H^+$ ions drives the dissociation equlibrium to the left.

Exercise

As you learned in Example 8, a 0.225 M solution of ethylamine ($CH_3CH_2NH_2$, p$K_b$ = 3.19) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

1. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
2. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

**Answer**

1. 11.16
2. 1.3%

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid ($BH^+$). The general equation for the ionization of a weak base is as follows:

$$B_{(aq)} + H_2O_{(l)} \leftrightharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{16.6.3}$$

If the equilibrium constant for the reaction as written in Equation 16.6.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = 1/K_b = 10^5$. Adding a strong base such as $OH^-$ to the solution therefore causes the equilibrium in Equation 16.6.3 to shift to the left, consuming the added $OH^-$. As a result, the $OH^-$ ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the $OH^-$ ion concentration, the reaction will proceed to the left to counteract the stress.

If the p$K_b$ of the base is 5.0, the p$K_a$ of its conjugate acid is p$K_a$ = p$K_w$ − p$K_b$ = 14.0 – 5.0 = 9.0. Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+_{(aq)} + H_2O_{(l)} \leftrightharpoons B_{(aq)} + H_3O^+_{(aq)} \tag{16.6.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 16.6.4 shifts to the left. As a result, the $H^+$ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb $H^+$ and $OH^-$ ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the *pH range* over which they can maintain a more or less constant pH and by their buffer capacityThe amount of strong acid or strong base that a buffer solution can absorb before the pH changes dramatically., the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on *K*), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 16.6.1, when NaOH is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

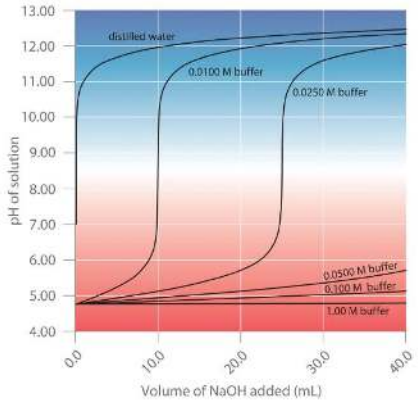



Figure 16.6.1 Effect of Buffer Concentration on the Capacity of a Buffer A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M NaOH to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of NaOH solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the NaOH solution results in only a relatively small change in pH.

## Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the $pK_a$ or $pK_b$ of the weak acid or weak base. The procedure is analogous to that used in Example 14 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \rightleftharpoons H^+ + A^-$ for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{16.6.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{16.6.6}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) = -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{16.6.7}$$

Replacing the negative logarithms in Equation 16.60,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{16.6.8}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{16.6.9}$$

Equation 16.6.8 and Equation 16.6.9 are both forms of the Henderson-Hasselbalch equationA rearranged version of the equilibrium constant expression that provides a direct way to calculate the pH of a buffer solution: pH = $pK_a$ + log([base]/[acid])., named after the two early-20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch equation may be limited to solutions whose concentrations are at least 100 times greater than their $K_a$ values.

There are three special cases where the Henderson-Hasselbalch equation is easily interpreted without the need for calculations:

1. **[base] = [acid].** Under these conditions, [base]/[acid] = 1 in Equation 16.6.9. Because log 1 = 0, pH = $pK_a$, *regardless of the actual concentrations of the acid and base*. Recall from Section 16.5 that this corresponds to the midpoint in the titration of a weak acid or a weak base.
2. **[base]/[acid] = 10.** In Equation 16.6.9, because log 10 = 1, pH = $pK_a$ + 1.
3. **[base]/[acid] = 100.** In Equation 16.6.9, because log 100 = 2, pH = $pK_a$ + 2.

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = $pK_a$ − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

### Note the Pattern

If [base] = [acid] for a buffer, then pH = $pK_a$. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

### Example 16.6.2

What is the pH of a solution that contains

1. 0.135 M $HCO_2H$ and 0.215 M $HCO_2Na$? (The $pK_a$ of formic acid is 3.75.)
2. 0.0135 M $HCO_2H$ and 0.0215 M $HCO_2Na$?
3. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The $pK_b$ of pyridine is 8.77.)

**Given:** concentration of acid, conjugate base, and $pK_a$; concentration of base, conjugate acid, and $pK_b$

**Asked for:** pH

**Strategy:**

Substitute values into either form of the Henderson-Hasselbalch equation (Equation 16.61 or Equation 16.62) to calculate the pH.

**Solution:**

1. According to the Henderson-Hasselbalch equation, the pH of a solution that contains both a weak acid and its conjugate base is pH = $pK_a$ + log([$A^-$]/[HA]). Inserting the given values into the equation,

   $$pH = 3.75 + \log\left(\frac{0.215}{0.135}\right) = 3.75 + \log 1.593 = 3.95$$

   This result makes sense because the [$A^-$]/[HA] ratio is between 1 and 10, so the pH of the buffer must be between the $pK_a$ (3.75) and $pK_a$ + 1, or 4.75.

2. This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch equation,

   $$pH = 3.75 + \log\left(\frac{0.0215}{0.0135}\right) = 3.75 + \log 1.593 = 3.95$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends *only* on the *ratio* of the concentrations of the conjugate base and the acid, *not* on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

3. In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion ($HPy^+$). We will therefore use Equation 16.62, the more general form of the Henderson-Hasselbalch equation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and [acid] = $[HPy^+]$ = 0.234 M. We also are given $pK_b$ = 8.77 for pyridine, but we need $pK_a$ for the pyridinium ion. Recall from Equation 16.2.10 that the $pK_b$ of a weak base and the $pK_a$ of its conjugate acid are related: $pK_a + pK_b = pK_w$. Thus $pK_a$ for the pyridinium ion is $pK_w - pK_b$ = 14.00 − 8.77 = 5.23. Substituting this $pK_a$ value into the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) = 5.23 + \log\left(\frac{0.119}{0.234}\right) = 5.23 - 0.294 = 4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the $pK_a$ (5.23) and $pK_a$ − 1, or 4.23.

Exercise

What is the pH of a solution that contains

1. 0.333 M benzoic acid and 0.252 M sodium benzoate?
2. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The $pK_a$ of benzoic acid is 4.20, and the $pK_b$ of trimethylamine is also 4.20.

**Answer**

1. 4.08
2. 9.68

The Henderson-Hasselbalch equation can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 16.

### Example 16.6.3

The buffer solution in Example 15 contained 0.135 M $HCO_2H$ and 0.215 M $HCO_2Na$ and had a pH of 3.95.

1. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
2. What is the final pH if 5.00 mL of 1.00 M NaOH are added?

**Given:** composition and pH of buffer; concentration and volume of added acid or base

**Asked for:** final pH

**Strategy:**

**A** Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 14. Then calculate the amount of acid or base added.

**B** Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch equation (Equation 16.6.9) to obtain the pH.

**Solution:**

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

1. **A** We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100 \cancel{mL}\left(\frac{0.135\ mmol\ HCO_2H}{\cancel{mL}}\right) = 13.5\ mmol\ HCO_2H$$

$$100 \cancel{mL}\left(\frac{0.215\ mmol\ HCO_2^-}{\cancel{mL}}\right) = 21.5\ mmol\ HCO_2^-$$

The millimoles of $H^+$ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00 \cancel{mL}\left(\frac{1.00\ mmol\ H^+}{\cancel{mL}}\right) = 5.00\ mmol\ H^+$$

**B** Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$HCO^{2-}_{(aq)} + H^+_{(aq)} \rightarrow HCO_2H_{(aq)}$$

| $HCO_2^-(aq) + H^+(aq) \rightarrow HCO_2H(aq)$ | | | |
|---|---|---|---|
| | $[HCO_2^-]$ | $[H^+]$ | $[HCO_2H]$ |
| initial | 21.5 mmol | 5.00 mmol | 13.5 mmol |
| change | −5.00 mmol | −5.00 mmol | +5.00 mmol |
| final | 16.5 mmol | ~0 mmol | 18.5 mmol |

The final amount of $H^+$ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 14 or the Henderson–Hasselbach equation. Because we have performed *many* equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch equation requires the concentrations of $HCO_2^-$ and $HCO_2H$, which can be calculated using the number of millimoles ($n$) of each and the total volume ($V_T$). Substituting these values into the Henderson-Hasselbalch equation,

$$pH = pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right)$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) = 3.75\ - 0.050 = 3.70$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of $HCO_2^-$ to $HCO_2H$ is slightly less than 1, so the pH should be between the $pK_a$ and $pK_a - 1$.

1. **A** The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of $HCO_2H$ and 21.5 mmol of $HCO_2^-$. The number of millimoles of $OH^-$ in 5.00 mL of 1.00 M NaOH is as follows:

$$5.00 \cancel{mL}\left(\frac{1.00\ mmol\ H^+}{\cancel{mL}}\right) = 5.00\ mmol\ H^+$$

**B** With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

| $HCO_2H(aq) + OH^-(aq) \rightarrow HCO_2^-(aq) + H_2O(l)$ | | | |
|---|---|---|---|
| | $[HCO_2H]$ | $[OH^-]$ | $[HCO_2^-]$ |
| initial | 13.5 mmol | 5.00 mmol | 21.5 mmol |
| change | −5.00 mmol | −5.00 mmol | +5.00 mmol |
| final | 8.5 mmol | ~0 mmol | 26.5 mmol |

The final amount of $OH^-$ in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both $HCO_2^-$ and $HCO_2H$ into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) = 3.75 + 0.494 = 4.24$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the p$K_a$ and p$K_a$ + 1, as expected for a solution with a $HCO_2^-$/$HCO_2H$ ratio between 1 and 10.

Exercise

The buffer solution from Example 15 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

1. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
2. What is the final pH if 12.0 mL of 1.5 M HCl are added?

**Answer**

1. 5.30
2. 4.42

## Note the Pattern

Only the *amounts* (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch equation, *not* their concentrations.

## Note the Pattern

The most effective buffers contain equal concentrations of an acid and its conjugate base.

The results obtained in Example 16 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or NaOH solution to 100 mL of an *un*buffered solution at pH 3.95 (corresponding to $1.1 \times 10^{-4}$ M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M NaOH would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 16.6.2 for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to $CH_3CO_2H$ from 1:1 reduces the buffer capacity of the solution.

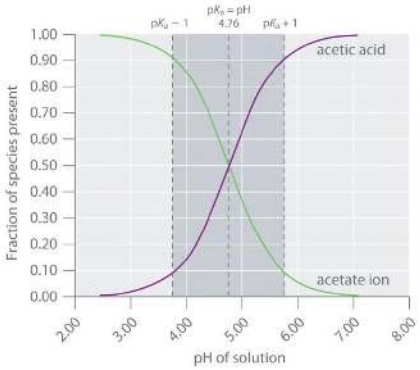



Figure 16.6.2 Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to pH = p$K_a$ ± 1).

## The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 16.6.3. As indicated by the labels, the region around p$K_a$ corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the p$K_a$ to approximately a pH value of 1 unit greater than the p$K_a$, which is why buffer solutions usually have a pH that is within ±1 pH units of the p$K_a$ of the acid component of the buffer.

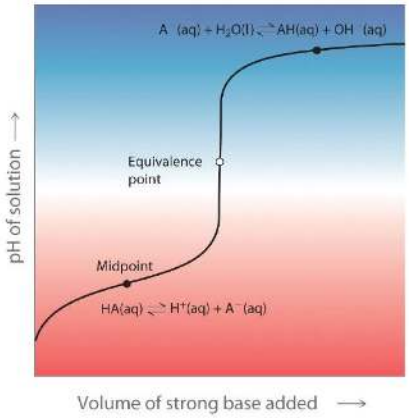



Figure 16.6.3 The Relationship between Titration Curves and **Buffers**This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to $K_a$. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to $K_b$. However, we can calculate either $K_a$ or $K_b$ from the other because they are related by $K_w$.

## Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $CO_2/HCO_3^-$ system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the $CO_2/HCO_3^-$ buffer system is usually written as follows:

$$H_2CO_{3(aq)} \leftrightharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{16.6.10}$$

with $K_a = 4.5 \times 10^{-7}$ and p$K_a$ = 6.35 at 25°C. In fact, Equation 16.6.10 is a grossly oversimplified version of the $CO_2/HCO_3^-$ system because a solution of $CO_2$ in water contains only rather small amounts of $H_2CO_3$. Thus Equation 16.6.10 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C. As shown in Equation 16.6.11, $CO_2$ is in equilibrium with $H_2CO_3$, but the equilibrium lies far to the left, with an $H_2CO_3/CO_2$ ratio less than 0.01 under most conditions:

$$CO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_2CO_{3(aq)} \tag{16.6.11}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true p$K_a$ of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a $K_a$ of $2.0 \times 10^{-4}$, which makes it a much stronger acid than Equation 16.6.10 suggests. Adding Equation 16.6.10 and Equation 16.6.11 and canceling $H_2CO_3$ from both sides give the following overall equation for the reaction of $CO_2$ with water to give a proton and the bicarbonate ion:

$$CO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_2CO_{3(aq)} \tag{16.6.12a}$$

with $K' = 4.0 \times 10^{-3} (37°C)$

$$H_2CO_{3(aq)} \leftrightharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{16.6.12b}$$

with $K_a = 2.0 \times 10^{-4} (37°C)$

$$CO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{16.6.12c}$$

with $K = 8.0 \times 10^{-7} (37°C)$

The $K$ value for the reaction in Equation 16.6.12 is the product of the *true* ionization constant for carbonic acid ($K_a$) and the equilibrium constant ($K$) for the reaction of $CO_2$(aq) with water to give carbonic acid. The equilibrium equation for the reaction of $CO_2$ with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{16.6.13}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law, $[CO_2] = kP(CO_2)$ where $k$ is the Henry's law constant for $CO_2$, which is $3.0 \times 10^{-5}$ M/mmHg at 37°C. (For more information about Henry's law, see Section 13.4 .) Substituting this expression for $[CO_2]$ in Equation 16.6.13,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})} \tag{16.6.14}$$

where $P(CO_2)$ is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{16.6.15}$$

Thus the pH of the solution depends on both the $CO_2$ pressure over the solution and $[HCO_3^-]$. Figure 16.6.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of $P(CO_2)$ with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

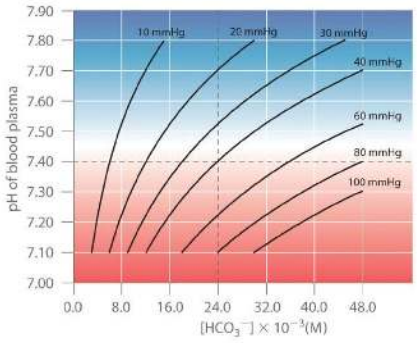



Figure 16.6.4 Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of $P(CO_2)$Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of $P(CO_2)$ indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines.

According to Equation 16.6.12, adding a strong acid to the $CO_2/HCO_3^-$ system causes $[HCO_3^-]$ to decrease as $HCO_3^-$ is converted to $CO_2$. Excess $CO_2$ is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in $P(CO_2)$. Because the change in $[HCO_3^-]/P(CO_2)$ is small, Equation 16.6.15 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the $OH^-$ reacts with $CO_2$ to form $[HCO_3^-]$, but $CO_2$ is replenished by the body, again limiting

the change in both $[HCO_3^-]/P(CO_2)$ and pH. The $CO_2/HCO_3^-$ buffer system is an example of an *open* system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower $P(CO_2)$ at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in $P(CO_2)$ are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

## Summary

**Buffers** are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base ($A^-$). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the **common ion effect**. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the $K_a$ or $K_b$), whereas its **buffer capacity** depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the **Henderson-Hasselbalch equation**, which is valid for solutions whose concentrations are at least 100 times greater than their $K_a$ values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $CO_2/HCO_3^-$ system, which dominates the buffering action of blood plasma.

## Key Equations

**Henderson-Hasselbalch equation**

Equation 16.6.8:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Equation 16.6.9:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

## Key Takeaway

- The common ion effect allows solutions to act as buffers, whose pH can be calculated using the Henderson-Hasselbalch equation.

## Conceptual Problems

1. Explain why buffers are crucial for the proper functioning of biological systems.
2. What is the role of a buffer in chemistry and biology? Is it correct to say that buffers prevent a change in $[H_3O^+]$? Explain your reasoning.
3. Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.
4. Which region of the titration curve of a weak acid or a weak base corresponds to the region of the smallest change in pH per amount of added strong acid or strong base?
5. If you were given a solution of sodium acetate, describe two ways you could convert the solution to a buffer.
6. Why are buffers usually used only within approximately one pH unit of the $pK_a$ or $pK_b$ of the parent weak acid or base?
7. The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?

1. a buffer
2. a solution of a salt of a weak base
3. a solution of a weak acid
4. diluting a strong base

8. Which of the following will produce a buffer solution? Explain your reasoning in each case.
    1. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
    2. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
    3. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl
    4. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M NaOH
    5. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M NaOH.
9. Which of the following will produce a buffer solution? Explain your reasoning in each case.
    1. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
    2. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
    3. mixing 100 mL of 0.1 M acetic acid and 100 mL of 0.1 M NaOH
    4. mixing 100 mL of 0.1 M acetic acid and 50 mL of 0.1 M NaOH
    5. mixing 100 mL of 0.1 M sodium acetate and 50 mL of 0.1 M acetic acid
10. Use the definition of $K_b$ for a weak base to derive the following expression, which is analogous to the Henderson-Hasselbalch equation but for a weak base (B) rather than a weak acid (HA):

$$pOH = pK_b - \log\left(\frac{[base]}{[acid]}\right) \tag{16.6.3}$$

11. Why do biological systems use overlapping buffer systems to maintain a constant pH?
12. The $CO_2/HCO_3^-$ buffer system of blood has an effective p$K_a$ of approximately 6.1, yet the normal pH of blood is 7.4. Why is $CO_2/HCO_3^-$ an effective buffer when the p$K_a$ is more than 1 unit below the pH of blood? What happens to the pH of blood when the $CO_2$ pressure increases? when the $O_2$ pressure increases?
13. Carbon dioxide produced during respiration is converted to carbonic acid ($H_2CO_3$). The p$K_{a1}$ of carbonic acid is 6.35, and its p$K_{a2}$ is 10.33. Write the equations corresponding to each p$K$ value and predict the equilibrium position for each reaction.

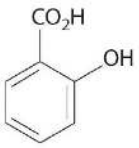
## Answer

1.
2.
3.
4.
5.
6.
7.
8.
9. 1. Not a buffer; the HCl completely neutralizes the sodium acetate to give acetic acid and NaCl(aq).
    2. Buffer; the HCl neutralizes only half of the sodium acetate to give a solution containing equal amounts of acetic acid and sodium acetate.
    3. Not a buffer; the NaOH completely neutralizes the acetic acid to give sodium acetate.
    4. Buffer; the NaOH neutralizes only half of the acetic acid to give a solution containing equal amounts of acetic acid and sodium acetate.
    5. Buffer; the solution will contain a 2:1 ratio of sodium acetate and acetic acid.
10.
11.
12.

13.

## Numerical Problems

1. Benzenesulfonic acid ($pK_a$ = 0.70) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:
    1. the pH of a 0.286 M solution of benzenesulfonic acid
    2. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M
2. Phenol has a $pK_a$ of 9.99. Calculate the following:
    1. the pH of a 0.195 M solution
    2. the percent increase in the concentration of phenol after adding enough solid sodium phenoxide (the sodium salt of the conjugate base) to give a total phenoxide concentration of 0.100 M
3. Salicylic acid is used in the synthesis of acetylsalicylic acid, or aspirin. One gram dissolves in 460 mL of water to create a saturated solution with a pH of 2.40.
    1. What is the $K_a$ of salicylic acid?
    2. What is the final pH of a saturated solution that is also 0.238 M in sodium salicylate?
    3. What is the final pH if 10.00 mL of 0.100 M HCl are added to 150.0 mL of the buffered solution?
    4. What is the final pH if 10.00 mL of 0.100 M NaOH are added to 150.0 mL of the buffered solution?



salicylic acid

4. An intermediate used in the synthesis of perfumes is valeric acid, also called pentanoic acid. The $pK_a$ of pentanoic acid is 4.84 at 25°C.
    1. What is the pH of a 0.259 M solution of pentanoic acid?
    2. Sodium pentanoate is added to make a buffered solution. What is the pH of the solution if it is 0.210 M in sodium pentanoate?
    3. What is the final pH if 8.00 mL of 0.100 M HCl are added to 75.0 mL of the buffered solution?
    4. What is the final pH if 8.00 mL of 0.100 M NaOH are added to 75.0 mL of the buffered solution?

## Answer

1.
2.
3. 1. $1.35 \times 10^{-3}$
    2. 4.03
    3. 3.88
    4. 4.30
4.

## Contributors

- Anonymous

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# CHAPTER OVERVIEW

## 17: Solubility and Complexation Equilibria


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# 17.1: Introduction

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Although Chapter 16 focused exclusively on acid–base equilibriums in aqueous solutions, equilibrium concepts can also be applied to many other kinds of reactions that occur in aqueous solution. In this chapter, we describe the equilibriums involved in the solubility of ionic compounds and the formation of complex ions.

Solubility equilibriums involving ionic compounds are important in fields as diverse as medicine, biology, geology, and industrial chemistry. Carefully controlled precipitation reactions of calcium salts, for example, are used by many organisms to produce structural materials, such as bone and the shells that surround mollusks and bird eggs. In contrast, uncontrolled precipitation reactions of calcium salts are partially or wholly responsible for the formation of scale in coffee makers and boilers, "bathtub rings," and kidney stones, which can be excruciatingly painful. The principles discussed in this chapter will enable you to understand how these apparently diverse phenomena are related. Solubility equilibriums are also responsible for the formation of caves and their striking features, such as stalactites and stalagmites, through a long process involving the repeated dissolution and precipitation of calcium carbonate. In addition to all of these phenomena, by the end of this chapter you will understand why barium sulfate is ideally suited for x-ray imaging of the digestive tract, and why soluble complexes of gadolinium can be used for imaging soft tissue and blood vessels using magnetic resonance imaging (MRI), even though most simple salts of both metals are toxic to humans.



**Scanning electron micrograph of kettle scale.** Hard water is a solution that consists largely of calcium and magnesium carbonate in $CO_2$-rich water. When the water is heated, $CO_2$ gas is released, and the carbonate salts precipitate from solution and produce a solid called *scale*.

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# 17.2: Determining the Solubility of Ionic Compounds

**Learning Objectives**

- To calculate the solubility of an ionic compound from its $K_{sp}$.

We begin our discussion of solubility and *complexation equilibriums*—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibriums, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

## The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as $S^{2-}$, $PO_4^{3-}$, and $CO_3^{2-}$, react with water to produce $OH^-$ and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{17.1.1}$$

The equilibrium constant for the dissolution of a sparingly soluble salt is the solubility product ($K_{sp}$)The equilibrium constant expression for the dissolution of a sparingly soluble salt that includes the concentration of a pure solid, which is a constant. of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. (For more information on the equilibrium constant expression, see Section 15.2.) The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{17.1.2a}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{sp} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{17.1.2b}$$

At 25°C and pH 7.00, $K_{sp}$ for calcium phosphate is $2.07 \times 10^{-33}$, indicating that the concentrations of $Ca^{2+}$ and $PO_4^{3-}$ ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of $K_{sp}$ for some common salts are listed in Table 17.1.1; they show that the magnitude of $K_{sp}$ varies dramatically for different compounds. Although $K_{sp}$ is not a function of pH in Equation 17.1, changes in pH can affect the solubility of a compound, as you will discover in Section 17.4.

### Note the Pattern

As with $K$, the concentration of a pure solid does not appear explicitly in $K_{sp}$.

**Table 17.1.1 Solubility Products for Selected Ionic Substances at 25°C**


https://chem.libretexts.org/@go/page/349761

| Solid | Color | $K_{sp}$ | | Solid | Color | $K_{sp}$ |
|---|---|---|---|---|---|---|
| **Acetates** | | | | **Iodides** | | |
| $Ca(O_2CCH_3)_2 \cdot 3H_2O$ | white | $4 \times 10^{-3}$ | | $Hg_2I_2$* | yellow | $5.2 \times 10^{-29}$ |
| **Bromides** | | | | $PbI_2$ | yellow | $9.8 \times 10^{-9}$ |
| AgBr | off-white | $5.35 \times 10^{-13}$ | | **Oxalates** | | |
| $Hg_2Br_2$* | yellow | $6.40 \times 10^{-23}$ | | $Ag_2C_2O_4$ | white | $5.40 \times 10^{-12}$ |
| **Carbonates** | | | | $MgC_2O_4 \cdot 2H_2O$ | white | $4.83 \times 10^{-6}$ |
| $CaCO_3$ | white | $3.36 \times 10^{-9}$ | | $PbC_2O_4$ | white | $4.8 \times 10^{-10}$ |
| $PbCO_3$ | white | $7.40 \times 10^{-14}$ | | **Phosphates** | | |
| **Chlorides** | | | | $Ag_3PO_4$ | white | $8.89 \times 10^{-17}$ |
| AgCl | white | $1.77 \times 10^{-10}$ | | $Sr_3(PO_4)_2$ | white | $4.0 \times 10^{-28}$ |
| $Hg_2Cl_2$* | white | $1.43 \times 10^{-18}$ | | $FePO_4 \cdot 2H_2O$ | pink | $9.91 \times 10^{-16}$ |
| $PbCl_2$ | white | $1.70 \times 10^{-5}$ | | **Sulfates** | | |
| **Chromates** | | | | $Ag_2SO_4$ | white | $1.20 \times 10^{-5}$ |
| $CaCrO_4$ | yellow | $7.1 \times 10^{-4}$ | | $BaSO_4$ | white | $1.08 \times 10^{-10}$ |
| $PbCrO_4$ | yellow | $2.8 \times 10^{-13}$ | | $PbSO_4$ | white | $2.53 \times 10^{-8}$ |
| **Fluorides** | | | | **Sulfides** | | |
| $BaF_2$ | white | $1.84 \times 10^{-7}$ | | $Ag_2S$ | black | $6.3 \times 10^{-50}$ |
| $PbF_2$ | white | $3.3 \times 10^{-8}$ | | CdS | yellow | $8.0 \times 10^{-27}$ |
| **Hydroxides** | | | | PbS | black | $8.0 \times 10^{-28}$ |
| $Ca(OH)_2$ | white | $5.02 \times 10^{-6}$ | | ZnS | white | $1.6 \times 10^{-24}$ |
| $Cu(OH)_2$ | pale blue | $1 \times 10^{-14}$ | | | | |
| $Mn(OH)_2$ | light pink | $1.9 \times 10^{-13}$ | | | | |
| $Cr(OH)_3$ | gray-green | $6.3 \times 10^{-31}$ | | | | |
| $Fe(OH)_3$ | rust red | $2.79 \times 10^{-39}$ | | | | |

*These contain the $Hg_2^{2+}$ ion.

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of *m*

*ass* of solute per 100 mL of solvent, $K_{sp}$, like *K*, is defined in terms of the *molar* concentrations of the component ions.



**A kidney stone.** Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2) \cdot H_2O$ and $Ca_3(PO_4)_2$.

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### Example 17.1.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)\cdot H_2O$, also written as $CaC_2O_4\cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is $7.36 \times 10^{-4}$ g/100 mL. Calculate its $K_{sp}$.

**Given:** solubility in g/100 mL

**Asked for:** $K_{sp}$

**Strategy:**

**A** Write the balanced dissolution equilibrium and the corresponding solubility product expression.

**B** Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate $K_{sp}$.

**Solution:**

**A** We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as $ox^{2-}$) are as follows:

$$Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l) \quad K_{sp} = [Ca^{2+}][ox^{2-}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

**B** Next we need to determine $[Ca^{2+}]$ and $[ox^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ Ca(O_2CCO_2)\cdot H_2O$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ Ca(O_2CCO_2\cdot)H_2O}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of $Ca^{2+}$ and $ox^{2-}$ ions are both $5.04 \times 10^{-5}$ M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise

One crystalline form of calcium carbonate ($CaCO_3$) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its $K_{sp}$.

**Answer:** $4.5 \times 10^{-9}$

### Note the Pattern

The reaction of weakly basic anions with $H_2O$ tends to make the actual solubility of many salts higher than predicted.

**A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction.** When a transparent crystal of calcite is placed over a page, we see *two* images of the letters.



Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of $K_{sp}$ can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations as we did in Chapter 15, remembering that the concentration of the pure solid is essentially constant.

### Example 17.1.2

We saw that the $K_{sp}$ for $Ca_3(PO_4)_2$ is $2.07 \times 10^{-33}$ at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

1. the molarity of ions produced in solution
2. the mass of salt that dissolves in 100 mL of water at 25°C

**Given:** $K_{sp}$

**Asked for:** molar concentration and mass of salt that dissolves in 100 mL of water

**Strategy:**

**A** Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.

**B** Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

**Solution:**

1. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 17.1) is shown in the following table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of $Ca^{2+}$ and 2 mol of $PO_4^{3-}$ ions are produced in solution. If we let $x$ equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

| **$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$** | | | |
|---|---|---|---|
| | $Ca_3(PO_4)_2$ | $[Ca^{2+}]$ | $[PO_4^{3-}]$ |
| initial | pure solid | 0 | 0 |
| change | — | $+3x$ | $+2x$ |
| final | pure solid | $3x$ | $2x$ |

Although the *amount* of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its *molar concentration* does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.1.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2$$
$$2.07 \times 10^{-33} = 108x^5$$
$$1.92 \times 10^{-35} = x^5$$
$$1.14 \times 10^{-7}\ \text{M} = x$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is $2x$ and $3x$, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

2. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water: $\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$

Exercise

The solubility product of silver carbonate ($Ag_2CO_3$) is $8.46 \times 10^{-12}$ at 25°C. Calculate the following:

1. the molarity of a saturated solution
2. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

**Answer**

1. $1.28 \times 10^{-4}$ M
2. 3.54 mg

## The Ion Product

The ion product ($Q$)A quantity that has precisely the same form as the solubility product for the dissolution of a sparingly soluble salt, except that the concentrations used are not necessarily equilibrium concentrations. of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient ($Q$) discussed for gaseous equilibriums in Chapter 15. Whereas $K_{sp}$ describes equilibrium concentrations, the ion product describes concentrations that are *not* necessarily equilibrium concentrations.

### Note the Pattern

The ion product $Q$ is analogous to the reaction quotient $Q$ for gaseous equilibriums.

As summarized in Figure 17.1.1 , there are three possible conditions for an aqueous solution of an ionic solid:

1. $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
2. $Q = K_{sp}$. The solution is saturated and at equilibrium.
3. $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

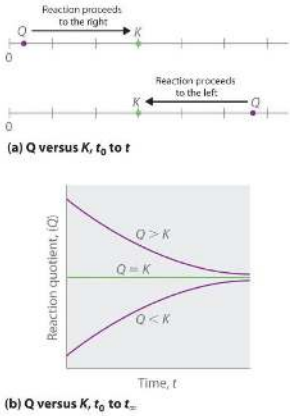



Figure 17.1.1 The Relationship between $Q$ and $K_{sp}$ If $Q$ is less than $K_{sp}$, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If $Q$ is greater than $K_{sp}$, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

### Example 17.1.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is $1.08 \times 10^{-10}$ at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M $Na_2SO_4$ is added to 100 mL of $3.2 \times 10^{-4}$ M $BaCl_2$? Recall that NaCl is highly soluble in water.

**Given:** $K_{sp}$ and volumes and concentrations of reactants

**Asked for:** whether precipitate will form

**Strategy:**

**A** Write the balanced equilibrium equation for the precipitation reaction and the expression for $K_{sp}$.

**B** Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product ($Q$).

**C** Compare the values of $Q$ and $K_{sp}$ to decide whether a precipitate will form.

**Solution:**

**A** The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08\times10^{-10}$$

**B** To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of $Ba^{2+}$ when the solutions are mixed is the total number of moles of $Ba^{2+}$ in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of $SO_4^{2-}$ after mixing is the total number of moles of $SO_4^{2-}$ in the original 10.0 mL of $Na_2SO_4$ solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate $Q$:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

**C** We now compare $Q$ with the $K_{sp}$. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

Exercise

The solubility product of calcium fluoride ($CaF_2$) is $3.45 \times 10^{-11}$. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a $2.0 \times 10^{-5}$ M solution of $Ca(NO_3)_2$, will $CaF_2$ precipitate?

**Answer:** yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

## The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases

—and vice versa—so that $K_{sp}$ is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. This dependency is another example of the common ion effect discussed in Section 16.6 : adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, *the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion*.The exceptions generally involve the formation of complex ions, which is discussed in Section 17.3 .

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is $1.14 \times 10^{-7}$ M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7}$ M $Ca^{2+}$ and $2 \times (1.14 \times 10^{-7}\ M) = 2.28 \times 10^{-7}$ M $PO_4^{3-}$, according to the stoichiometry shown in Equation 17.1.1 (neglecting hydrolysis to form $HPO_4^{2-}$ as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the $Ca^{2+}$ ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 17.1.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both $Ca^{2+}$ and $PO_4^{3-}$ until $Q = K_{sp}$.

### Note the Pattern

The common ion effect usually decreases the solubility of a sparingly soluble salt.

### Example 17.1.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

**Given:** concentration of $CaCl_2$ solution

**Asked for:** solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

**Strategy:**

**A** Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

**B** Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

**Solution:**

**A** The balanced equilibrium equation is given in the following table. If we let $x$ equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again $+3x$, and the change in $[PO_4^{3-}]$ is $+2x$. We can insert these values into the table.

| $Ca_3(PO_4)^2(s) = 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ | | | |
|---|---|---|---|
| | $Ca_3(PO_4)_2$ | $[Ca^{2+}]$ | $[PO_4^{3-}]$ |
| initial | pure solid | 0.20 | 0 |
| change | — | $+3x$ | $+2x$ |
| final | pure solid | $0.20 + 3x$ | $2x$ |

**B** The $K_{sp}$ expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07 \times 10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the $K_{sp}$ expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ \text{M} \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is $8.45 \times 10^{-12}$ at 25°C.

**Answer:** $2.9 \times 10^{-6}$ M (versus $1.3 \times 10^{-4}$ M in pure water)

## Summary

The equilibrium constant for a dissolution reaction, called the **solubility product ($K_{sp}$)**, is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of *mass* of solute per 100 mL of solvent, $K_{sp}$ is defined in terms of the *molar* concentrations of the component ions. In contrast, the **ion product (*Q*)** describes concentrations that are not necessarily equilibrium concentrations. Comparing *Q* and $K_{sp}$ enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

## Key Takeaway

- The solubility product ($K_{sp}$) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (*Q*) describes concentrations that are not necessarily at equilibrium.

## Conceptual Problems

1. Write an expression for $K_{sp}$ for each salt.
    1. AgI
    2. $CaF_2$
    3. $PbCl_2$
    4. $Ag_2CrO_4$
2. Some species are not represented in a solubility product expression. Why?
3. Describe the differences between *Q* and $K_{sp}$.
4. How can an ion product be used to determine whether a solution is saturated?
5. When using $K_{sp}$ to directly compare the solubilities of compounds, why is it important to compare only the $K_{sp}$ values of salts that have the same stoichiometry?
6. Describe the effect of a common ion on the solubility of a salt. Is this effect similar to the common ion effect found in buffers? Explain your answer.
7. Explain why the presence of $MgCl_2$ decreases the molar solubility of the sparingly soluble salt $MgCO_3$.

## Answers

1. 1. $K_{sp} = [Ag^+][I^-]$
    2. $K_{sp} = [Ca^{2+}][F^-]^2$
    3. $K_{sp} = [Pb^{2+}][Cl^-]^2$
    4. $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$
2. 
3. 
4. 
5. For a 1:1 salt, the molar solubility is simply $\sqrt{K_{sp}}$ ; for a 2:1 salt, the molar solubility is $\sqrt[3]{K_{sp}/4}$> Consequently, the magnitudes of $K_{sp}$ can be correlated with molar solubility *only* if the salts have the same stoichiometry.
6. 
7. Because of the common ion effect. Adding a soluble $Mg^{2+}$ salt increases $[Mg^{2+}]$ in solution, and Le Chatelier's principle predicts that this will shift the solubility equilibrium of $MgCO_3$ to the left, decreasing its solubility.

## Numerical Problems

1. Predict the molar solubility of each compound using the $K_{sp}$ values given in Table E3.
    1. $Cd(IO_3)_2$
    2. AgCN
    3. $HgI_2$
2. Predict the molar solubility of each compound using the $K_{sp}$ values given.
    1. $Li_3PO_4$: $2.37 \times 10^{-11}$
    2. $Ca(IO_3)_2$: $6.47 \times 10^{-6}$
    3. $Y(IO_3)_3$: $1.12 \times 10^{-10}$
3. A student prepared 750 mL of a saturated solution of silver sulfate ($Ag_2SO_4$). How many grams of $Ag_2SO_4$ does the solution contain? $K_{sp} = 1.20 \times 10^{-5}$.
4. Given the $K_{sp}$ values in Table 17.1.1 and Table E3, predict the molar concentration of each species in a saturated aqueous solution.
    1. silver bromide
    2. lead oxalate
    3. iron(II) carbonate
    4. silver phosphate
    5. copper(I) cyanide
5. Given the $K_{sp}$ values in Table 17.1.1 and Table E3, predict the molar concentration of each species in a saturated aqueous solution.
    1. copper(I) chloride
    2. lanthanum(III) iodate
    3. magnesium phosphate
    4. silver chromate
    5. strontium sulfate
6. Silicon dioxide, the most common binary compound of silicon and oxygen, constitutes approximately 60% of Earth's crust. Under certain conditions, this compound can react with water to form silicic acid, which can be written as either $H_4SiO_4$ or $Si(OH)_4$. Write a balanced chemical equation for the dissolution of $SiO_2$ in basic solution. Write an equilibrium constant expression for the reaction.
7. The $K_{sp}$ of $Mg(OH)_2$ is $5.61 \times 10^{-12}$. If you tried to dissolve 24.0 mg of $Mg(OH)_2$ in 250 mL of water and then filtered the solution and dried the remaining solid, what would you predict to be the mass of the undissolved solid? You discover that only 1.0 mg remains undissolved. Explain the difference between your expected value and the actual value.
8. The $K_{sp}$ of lithium carbonate is $8.15 \times 10^{-4}$. If 2.34 g of the salt is stirred with 500 mL of water and any undissolved solid is filtered from the solution and dried, what do you predict to be the mass of the solid? You discover that all of your sample dissolves. Explain the difference between your predicted value and the actual value.
9. You have calculated that 24.6 mg of $BaSO_4$ will dissolve in 1.0 L of water at 25°C. After adding your calculated amount to 1.0 L of water and stirring for several hours, you notice that the solution contains undissolved solid. After carefully filtering the solution and drying the solid, you find that 22.1 mg did not dissolve. According to your measurements, what is the $K_{sp}$ of barium sulfate?
10. In a saturated silver chromate solution, the molar solubility of chromate is $6.54 \times 10^{-5}$. What is the $K_{sp}$?
11. A saturated lead(II) chloride solution has a chloride concentration of $3.24 \times 10^{-2}$ mol/L. What is the $K_{sp}$?
12. From the solubility data given, calculate $K_{sp}$ for each compound.
    1. AgI: $2.89 \times 10^{-7}$ g/100 mL
    2. $SrF_2$: $1.22 \times 10^{-2}$ g/100 mL

3. $Pb(OH)_2$: 78 mg/500 mL
4. $BiAsO_4$: 14.4 mg/2.0 L

13. From the solubility data given, calculate $K_{sp}$ for each compound.

    1. $BaCO_3$: 10.0 mg/500 mL
    2. $CaF_2$: 3.50 mg/200 mL
    3. $Mn(OH)_2$: $6.30 \times 10^{-4}$ g/300 mL
    4. $Ag_2S$: $1.60 \times 10^{-13}$ mg/100 mL

14. Given the following solubilities, calculate $K_{sp}$ for each compound.

    1. $BaCO_3$: $7.00 \times 10^{-5}$ mol/L
    2. $CaF_2$: 1.70 mg/100 mL
    3. $Pb(IO_3)_2$: 2.30 mg/100 mL
    4. $SrC_2O_4$: $1.58 \times 10^{-7}$mol/L

15. Given the following solubilities, calculate $K_{sp}$ for each compound.

    1. $Ag_2SO_4$: $4.2 \times 10^{-1}$ g/100 mL
    2. $SrSO_4$: $1.5 \times 10^{-3}$ g/100 mL
    3. $CdC_2O_4$: $6.0 \times 10^{-3}$ g/100 mL
    4. $Ba(IO_3)_2$: $3.96 \times 10^{-2}$ g/100 mL

16. The $K_{sp}$ of the phosphate fertilizer $CaHPO_4 \cdot 2H_2O$ is $2.7 \times 10^{-7}$ at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 3.0 L of water at this temperature?

17. The $K_{sp}$ of zinc carbonate monohydrate is $5.5 \times 10^{-11}$ at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 2.0 L of water at this temperature?

18. Silver nitrate eye drops were formerly administered to newborn infants to guard against eye infections contracted during birth. Although silver nitrate is highly water soluble, silver sulfate has a $K_{sp}$ of $1.20 \times 10^{-5}$ at 25°C. If you add 25.0 mL of 0.015 M $AgNO_3$ to 150 mL of $2.8 \times 10^{-3}$ M $Na_2SO_4$, will you get a precipitate? If so, what will its mass be?

19. Use the data in Table E3 to predict whether precipitation will occur when each pair of solutions is mixed.

    1. 150 mL of 0.142 M $Ba(NO_3)_2$ with 200 mL of 0.089 M NaF
    2. 250 mL of 0.079 M $K_2CrO_4$ with 175 mL of 0.087 M $CaCl_2$
    3. 300 mL of 0.109 M $MgCl_2$ with 230 mL of 0.073 M $Na_2(C_2O_4)$

20. What is the maximum volume of 0.048 M $Pb(NO_3)_2$ that can be added to 250 mL of 0.10 M NaSCN before precipitation occurs? $K_{sp} = 2.0 \times 10^{-5}$ for $Pb(SCN)_2$.

21. Given 300 mL of a solution that is 0.056 M in lithium nitrate, what mass of solid sodium carbonate can be added before precipitation occurs (assuming that the volume of solution does not change after adding the solid)? $K_{sp} = 8.15 \times 10^{-4}$ for $Li_2CO_3$.

22. Given the information in the following table, calculate the molar solubility of each sparingly soluble salt in 0.95 M $MgCl_2$.

| Saturated Solution | $K_{sp}$ |
|---|---|
| $MgCO_3 \cdot 3H_2O$ | $2.4 \times 10^{-6}$ |
| $Mg(OH)_2$ | $5.6 \times 10^{-12}$ |
| $Mg_3(PO_4)_2$ | $1.04 \times 10^{-24}$ |

## Answers

1. 1. $1.84 \times 10^{-3}$ M
   2. $7.73 \times 10^{-9}$ M
   3. $1.9 \times 10^{-10}$ M

2.

3. 3.37 g

4.

5. 1. $4.15 \times 10^{-4}$ M
   2. $7.26 \times 10^{-4}$ M
   3. $6.26 \times 10^{-6}$ M
   4. $6.54 \times 10^{-5}$ M
   5. $5.86 \times 10^{-4}$ M

6.

7. 22.4 mg; a secondary reaction occurs, where $OH^-$ from the dissociation of the salt reacts with $H^+$ from the dissociation of water. This reaction causes further dissociation of the salt (Le Chatelier's principle).

8.

9. $1.2 \times 10^{-10}$

10.

11. $1.70 \times 10^{-5}$

12.

13.

14.

15. 1. $8.8 \times 10^{-6}$
    2. $6.7 \times 10^{-9}$
    3. $9.0 \times 10^{-8}$
    4. $2.16 \times 10^{-9}$

16.

17. $7.4 \times 10^{-6}$ M; 2.1 mg

18.

19. Precipitation will occur in all cases.

20.

21. 8.27 g

22.

## Contributors

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Modified by Joshua B. Halpern

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# 17.3: Factors That Affect Solubility

**Learning Objectives**

- To understand the factors that determine the solubility of ionic compounds.

The solubility product of an ionic compound describes the concentrations of *ions* in equilibrium with a solid, but what happens if some of the cations become associated with anions rather than being completely surrounded by solvent? Then predictions of the total solubility of the compound based on the assumption that the solute exists solely as discrete ions would differ substantially from the actual solubility, as would predictions of ionic concentrations. In general, four situations explain why the solubility of a compound may be other than expected: ion pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH. The first two situations are described in this section, the formation of complex ions is discussed in Section 17.3 , and changes in pH are discussed in Section 17.4.

## Ion-Pair Formation

An ion pairA cation and an anion that are in intimate contact in solution rather than separated by solvent. An ion pair can be viewed as a species that is intermediate between the ionic solid and the completely dissociated ions in solution. consists of a cation and an anion that are in intimate contact in solution, rather than separated by solvent (Figure 17.2.1). The ions in an ion pair are held together by the same attractive electrostatic forces that we discussed in Chapter 4 for ionic solids. As a result, the ions in an ion pair migrate as a single unit, whose net charge is the sum of the charges on the ions. In many ways, we can view an ion pair as a species intermediate between the ionic solid (in which each ion participates in many cation–anion interactions that hold the ions in a rigid array) and the completely dissociated ions in solution (where each is fully surrounded by water molecules and free to migrate independently).

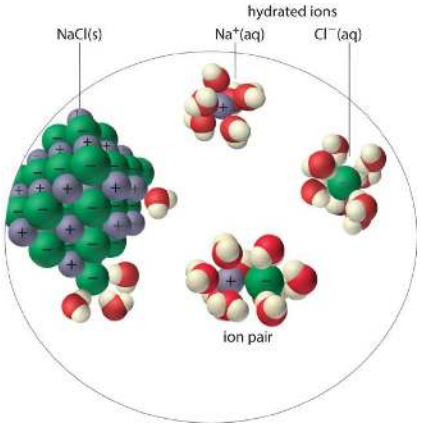



Figure 17.2.1 Ion-Pair **Formation**In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

As illustrated for calcium sulfate in the following equation, a second equilibrium must be included to describe the solubility of salts that form ion pairs:

$$\underset{\text{ion pair}}{\mathrm{CaSO_4(s) \rightleftharpoons Ca^{2+} \cdot SO_4^{2-}(aq)}} \rightleftharpoons \mathrm{Ca^{2+}(aq) + SO_4^{2-}(aq)} \tag{17.2.1}$$

The ion pair is represented by the symbols of the individual ions separated by a dot, which indicates that they are associated in solution. The formation of an ion pair is a dynamic process, just like any other equilibrium, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.

Ion-pair formation can have a major effect on the measured solubility of a salt. For example, the measured $K_{sp}$ for calcium sulfate is $4.93 \times 10^{-5}$ at 25°C. The solubility of $CaSO_4$ should be $7.02 \times 10^{-3}$ M if the only equilibrium involved were as follows:

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{17.2.2}$$

In fact, the experimentally measured solubility of calcium sulfate at 25°C is $1.6 \times 10^{-2}$ M, almost twice the value predicted from its $K_{sp}$. The reason for the discrepancy is that the concentration of ion pairs in a saturated $CaSO_4$ solution is almost as high as the concentration of the hydrated ions. Recall that the magnitude of attractive electrostatic interactions is greatest for small, highly charged ions. Hence ion pair formation is most important for salts that contain $M^{2+}$ and $M^{3+}$ ions, such as $Ca^{2+}$ and $La^{3+}$, and is relatively unimportant for salts that contain monopositive cations, except for the smallest, $Li^+$. We therefore expect a saturated solution of $CaSO_4$ to contain a high concentration of ion pairs and its solubility to be greater than predicted from its $K_{sp}$.

### Note the Pattern

The formation of ion pairs increases the solubility of a salt.

## Incomplete Dissociation

A molecular solute may also be more soluble than predicted by the measured concentrations of ions in solution due to *incomplete dissociation*. This is particularly common with weak organic acids. (For more information about weak organic acids, see Chapter 16 ). Although strong acids (HA) dissociate completely into their constituent ions ($H^+$ and $A^-$) in water, weak acids such as carboxylic acids do not ($K_a = 1.5 \times 10^{-5}$). However, the molecular (undissociated) form of a weak acid (HA) is often quite soluble in water; for example, acetic acid ($CH_3CO_2H$) is completely miscible with water. Many carboxylic acids, however, have only limited solubility in water, such as benzoic acid ($C_6H_5CO_2H$), with $K_a = 6.25 \times 10^{-5}$. Just as with calcium sulfate, we need to include an additional equilibrium to describe the solubility of benzoic acid:

$$C_6H_5CO_2H_{(s)} \rightleftharpoons C_6H_5CO_2H_{(aq)} \rightleftharpoons C_6H_5CO^-_{2(aq)} + H^+_{(aq)} \tag{17.2.3}$$

In a case like this, measuring only the concentration of the ions grossly underestimates the total concentration of the organic acid in solution. In the case of benzoic acid, for example, the pH of a saturated solution at 25°C is 2.85, corresponding to $[H^+] = [C_6H_5CO_2^-] = 1.4 \times 10^{-3}$ M. The total concentration of benzoic acid in the solution, however, is $2.8 \times 10^{-2}$ M. Thus approximately 95% of the benzoic acid in solution is in the form of hydrated neutral molecules—$C_6H_5CO_2H$(aq)—and only about 5% is present as the dissociated ions (Figure 17.2.2).

### Note the Pattern

Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.

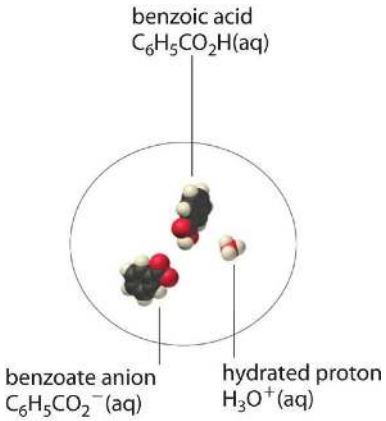



Figure 17.2.2 Incomplete Dissociation of a Molecular Solute In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. ($H_2O$ molecules are omitted for clarity.)

Although ion pairs, such as $Ca^{2+}{\cdot}SO_4^{2-}$, and undissociated electrolytes, such as $C_6H_5CO_2H$, are both electrically neutral, there is a major difference in the forces responsible for their formation. Simple electrostatic attractive forces between the cation and the anion hold the ion pair together, whereas a polar covalent O−H bond holds together the undissociated electrolyte.

### Summary

There are four explanations why the solubility of a compound can differ from the solubility indicated by the concentrations of ions: (1) **ion pair** formation, in which an anion and a cation are in intimate contact in solution and not separated by solvent, (2) the

incomplete dissociation of molecular solutes, (3) the formation of complex ions, and (4) changes in pH. An ion pair is held together by electrostatic attractive forces between the cation and the anion, whereas incomplete dissociation results from intramolecular forces, such as polar covalent O–H bonds.

### Key Takeaway

- Ion-pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH all affect solubility.

### Conceptual Problems

1. Do you expect the actual molar solubility of $LaPO_4$ to be greater than, the same as, or less than the value calculated from its $K_{sp}$? Explain your reasoning.
2. Do you expect the difference between the calculated molar solubility and the actual molar solubility of $Ca_3(PO_4)_2$ to be greater than or less than the difference in the solubilities of $Mg_3(PO_4)_2$? Why?
3. Write chemical equations to describe the interactions in a solution that contains $Mg(OH)_2$, which forms ion pairs, and in one that contains propanoic acid ($CH_3CH_2CO_2H$), which forms a hydrated neutral molecule.
4. Draw representations of $Ca(IO_3)_2$ in solution
    1. as an ionic solid.
    2. in the form of ion pairs.
    3. as discrete ions.

### Numerical Problem

1. Ferric phosphate has a molar solubility of $5.44 \times 10^{-16}$ in 1.82 M $Na_3PO_4$. Predict its $K_{sp}$. The actual $K_{sp}$ is $1.3 \times 10^{-22}$. Explain this discrepancy.

### Answer

1. $9.90 \times 10^{-16;}$ the solubility is much higher than predicted by $K_{sp}$ due to the formation of ion pairs (and/or phosphate complexes) in the sodium phosphate solution.

### Contributors

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# 17.4: The Formation of Complex Ions

**Learning Objectives**

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as $Cu^{2+}$ or $Ru^{3+}$, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated $Cu^{2+}$ ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than $H_2O$, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 17.4.1. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.




Figure 17.4.1: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated $Cu^{2+}$ ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than $H_2O$, replaces water molecules from the hydrated $Cu^{2+}$ ion. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0.

## The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to $Cu^{2+}$ for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1 \tag{17.4.1}$$

$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2 \tag{17.4.2}$$

$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3 \tag{17.4.3}$$

$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4 \tag{17.4.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated $Cu^{2+}$ ion contains six $H_2O$ ligands, but the complex ion that is produced contains only four $NH_3$ ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{17.4.5}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant ($K_f$)**. The equilibrium constant expression for $K_f$ has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{17.4.6}$$

> *The formation constant ($K_f$) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as $Cu^{2+}$ for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, $K_f$), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 17.4.1.

Table 17.4.1: Formation Constants for Selected Complex Ions in Aqueous Solution*

| | Complex Ion | Equilibrium Equation | $K_f$ |
|---|---|---|---|
| **Ammonia Complexes** | $[Ag(NH_3)_2]^+$ | $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ | $1.1 \times 10^7$ |
| | $[Cu(NH_3)_4]^{2+}$ | $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ | $2.1 \times 10^{13}$ |
| | $[Ni(NH_3)_6]^{2+}$ | $Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$ | $5.5 \times 10^8$ |
| **Cyanide Complexes** | $[Ag(CN)_2]^-$ | $Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$ | $1.1 \times 10^{18}$ |
| | $[Ni(CN)_4]^{2-}$ | $Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$ | $2.2 \times 10^{31}$ |
| | $[Fe(CN)_6]^{3-}$ | $Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$ | $1 \times 10^{42}$ |
| **Hydroxide Complexes** | $[Zn(OH)_4]^{2-}$ | $Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$ | $4.6 \times 10^{17}$ |
| | $[Cr(OH)_4]^-$ | $Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$ | $8.0 \times 10^{29}$ |
| **Halide Complexes** | $[HgCl_4]^{2-}$ | $Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$ | $1.2 \times 10^{15}$ |
| | $[CdI_4]^{2-}$ | $Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$ | $2.6 \times 10^5$ |
| | $[AlF_6]^{3-}$ | $Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$ | $6.9 \times 10^{19}$ |
| **Other Complexes** | $[Ag(S_2O_3)_2]^{3-}$ | $Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$ | $2.9 \times 10^{13}$ |
| | $[Fe(C_2O_4)_3]^{3-}$ | $Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$ | $2.0 \times 10^{20}$ |

*Reported values are overall formation constants.
Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

## Example 17.4.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

**Given:** mass of $Cu^{2+}$ salt and volume and concentration of ammonia solution

**Asked for:** equilibrium concentration of $Cu^{2+}(aq)$

**Strategy:**

A. Calculate the initial concentration of $Cu^{2+}$ due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 17.4.5 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 17.4.6) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

**Solution**

Adding an ionic compound that contains $Cu^{2+}$ to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}$ (aq), as shown in Equation 17.4.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

**A** The initial concentration of $Cu^{2+}$ from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{\text{ g}}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1 \text{ mol}}{295.65 \cancel{\text{ g}}}\right)\left(\frac{1}{500 \cancel{\text{ mL}}}\right)\left(\frac{1000 \cancel{\text{ mL}}}{1 \text{ L}}\right) = 0.0846 \text{ M} \tag{17.4.7}$$

Because the stoichiometry of the reaction is four $NH_3$ to one $Cu^{2+}$, the amount of $NH_3$ required to react completely with the $Cu^{2+}$ is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large ($2.1 \times 10^{13}$), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into $Cu^{2+}$ and $NH_3$ until equilibrium has been reached. If we define $x$ as the amount of $Cu^{2+}$ produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is $-x$, and the change in the concentration of ammonia is $+4x$, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$\mathbf{Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}}$$

| | $[Cu^{2+}]$ | $[NH_3]$ | $[[Cu(NH_3)_4]^{2+}]$ |
|---|---|---|---|
| initial | 0.0846 | 1.00 | 0 |
| after complete reaction | 0 | 0.66 | 0.0846 |
| change | $+x$ | $+4x$ | $-x$ |
| final | $x$ | 0.66 + 4$x$ | 0.0846 − $x$ |

**B** Substituting the final concentrations into the expression for the formation constant (Equation 17.4.6) and assuming that $x$ << 0.0846, which allows us to remove $x$ from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \tag{17.4.8}$$

$$x = 2.1 \times 10^{-14} \tag{17.4.9}$$

The value of $x$ indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}$(aq) in a 1.00 M ammonia solution is therefore $2.1 \times 10^{-14}$ M.

**? Exercise 17.4.1**

The ferrocyanide ion {$[Fe(CN)_6]^{4-}$} is very stable, with a $K_f$ of $1 \times 10^{35}$. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

**Answer**

$1.2 \times 10^{-5}$ M

## The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a $K_{sp}$ of $5.35 \times 10^{-13}$ at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in

tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

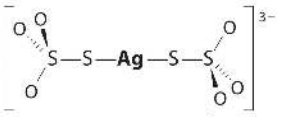
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)} \tag{17.4.10}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°C \tag{17.4.11}$$

The equilibrium lies far to the left, and the equilibrium concentrations of $Ag^+$ and $Br^-$ ions are very low ($7.31 \times 10^{-7}$ M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of $Ag^+$

The reaction of $Ag^+$ with thiosulfate is as follows:

$$Ag^{+}_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{17.4.12}$$

with

$$K_f = 2.9 \times 10^{13} \tag{17.4.13}$$

The magnitude of the equilibrium constant indicates that almost all $Ag^+$ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)} \quad K_{sp} = 5.35 \times 10^{-13} \tag{17.4.14}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)} \quad K_f = 2.9 \times 10^{13} \tag{17.4.15}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{sp}K_f = 15 \tag{17.4.16}$$

Comparing $K$ with $K_{sp}$ shows that the formation of the complex ion increases the solubility of AgBr by approximately $3 \times 10^{13}$. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large $K_f$, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

**Example 17.4.2**

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only $Ag^+$ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

**Given:** $K_{sp}$ of AgCl, $K_f$ of $AgCl_2^-$, and KCl concentration

**Asked for:** solubility of AgCl in water and in KCl solution with and without the formation of complex ions

**Strategy:**

A. Write the solubility product expression for AgCl and calculate the concentration of $Ag^+$ and $Cl^-$ in water.
B. Calculate the concentration of $Ag^+$ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

**Solution**

a. **A** If we let $x$ equal the solubility of AgCl, then at equilibrium [Ag+] = $[Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77 \times 10^{-10}$$
$$x = 1.33 \times 10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is $1.33 \times 10^{-5}$ M.

b. **B** If $x$ equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77 \times 10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to $K_{sp}$ and $K_f$ gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of $K_{sp}$ and $K_f$:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \tag{17.4.17}$$
$$Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \tag{17.4.18}$$
$$AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{17.4.19}$$

**D** If we let $x$ equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a $1.9 \times 10^{-5}$ M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is $10^5$ times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

## ? Exercise 17.4.2

Calculate the solubility of mercury(II) iodide ($HgI_2$) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

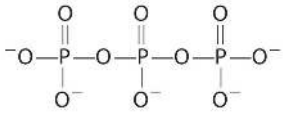
$K_{sp} = 2.9 \times 10^{-29}$ for $HgI_2$ and $K_f = 6.8 \times 10^{29}$ for $[HgI_4]^{2-}$.

**Answer**

a. $1.9 \times 10^{-10}$ M

b. 1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with $Ca^{2+}$ and $Mg^{2+}$, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



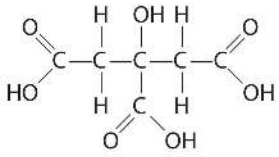
triphosphate

$$Ca^{2+}_{(aq)} + O_3POPO^{4-}_{4(aq)} \rightleftharpoons [Ca(O_3POPO_3)]^{2-}_{(aq)} \tag{17.4.20}$$

with

$$K_f = 4 \times 10^4 \tag{17.4.21}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of $Na^+$, but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the $^1H$ nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to "see" each of these separately (Figure 17.4.2). One of the most important metal ions for this application is $Gd^{3+}$, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}$(aq) is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

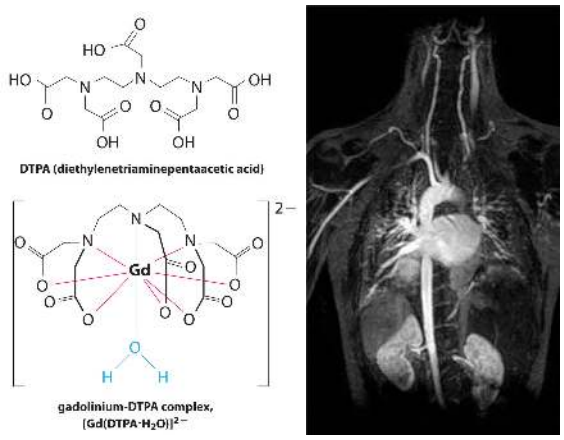



Figure 17.4.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

## Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large $K_f$. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant ($K_f$). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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# 17.5: Solubility and pH

**Learning Objectives**

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

## The Effect of Acid–Base Equilibriums on the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, $M^+A^-$, where $A^-$ is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

$$MA_{(s)} \rightleftharpoons M^+_{(aq)} + A^-_{(aq)} \tag{17.4.1a}$$

with

$$K_{sp} = [M^+][A^-] \tag{17.4.1b}$$

The anion can also react with water in a hydrolysis reaction:

$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HA_{(aq)} \tag{17.4.2}$$

Because of the reaction described in Equation 17.4.2, the predicted solubility of a sparingly soluble salt that has a basic anion such as $S^{2-}$, $PO_4^{3-}$, or $CO_3^{2-}$ is increased, as described in Section 17.1. If instead a strong acid is added to the solution, the added $H^+$ will react essentially completely with $A^-$ to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product ($Q = [M^+][A^-]$). According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence *an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid*. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a *strong* acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{17.4.3a}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{17.4.3b}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing $OH^-$ from solution:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \tag{17.4.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+_{(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + 2H_2O_{(l)} \tag{17.4.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 17.4.6 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, $CaF_2$ is a sparingly soluble salt:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)} \tag{17.4.7a}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{17.4.7b}$$

When strong acid is added to a saturated solution of $CaF_2$, the following reaction occurs:

$$H^+_{(aq)} + F^-_{(aq)} \rightleftharpoons HF_{(aq)} \tag{17.4.8}$$

Because the forward reaction decreases the fluoride ion concentration, more $CaF_2$ dissolves to relieve the stress on the system. The net reaction of $CaF_2$ with strong acid is thus

$$CaF_{2(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + 2HF_{(aq)} \tag{17.4.9}$$

Example 7 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

### Note the Pattern

Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.

### Example 17.4.1

Lead oxalate ($PbC_2O_4$), lead iodide ($PbI_2$), and lead sulfate ($PbSO_4$) are all rather insoluble, with $K_{sp}$ values of $4.8 \times 10^{-10}$, $9.8 \times 10^{-9}$, and $2.53 \times 10^{-8}$, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

**Given:** $K_{sp}$ values for three compounds

**Asked for:** relative solubilities in acid solution

**Strategy:**

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

**Solution:**

The solubility equilibriums for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^-_{(aq)}$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of $PbI_2$ will not greatly affect its solubility; the acid will simply dissociate to form $H^+$(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid ($HO_2CCO_2H$), which is a weak diprotic acid ($pK_{a1}$ = 1.23 and $pK_{a2}$ = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C_2O^{2-}_{4(aq)} + H^+_{(aq)} \rightarrow HO_2CCO^-_{2(aq)}$$

$$HO_2CCO^-_{2(aq)} + H^+_{(aq)} \rightarrow HO_2CCO_2H_{(aq)}$$

These reactions will decrease $[C_2O_4{}^{2-}]$, causing more lead oxalate to dissolve to relieve the stress on the system.The $pK_a$ of $HSO_4{}^-$ (1.99) is similar in magnitude to the $pK_{a1}$ of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO^{2-}_{4(aq)} + H^+_{(aq)} \rightleftharpoons HSO^-_{4(aq)}$$

Because $HSO_4{}^-$ has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for $PbC_2O_4$.

Exercise

Which of the following insoluble salts—AgCl, $Ag_2CO_3$, $Ag_3PO_4$, and/or AgBr—will be substantially more soluble in 1.0 M $HNO_3$ than in pure water?

**Answer:** $Ag_2CO_3$ and $Ag_3PO_4$

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility equilibriums (part (a) in Figure 17.6). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \tag{17.4.10}$$

$$HCO^-_{3(aq)} \rightleftharpoons H + (aq) + CO^{2-}_{3(aq)} \tag{17.4.11}$$

$$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightleftharpoons CaCO_{3(s)} \tag{17.4.12}$$




Figure 17.4.1 The Chemistry of Cave Formation (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric $CO_2$, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in $CO_2$-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in $CO_2$-rich water rises toward Earth's surface or is otherwise heated, $CO_2$ gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 17.4.1):

$$Ca^{2+}_{(aq)} + 2HCO^-_{3(aq)} \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \tag{17.4.13}$$

The forward direction is the same reaction that produces the solid called *scale* in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.

When groundwater-containing atmospheric $CO_2$ (Equation 17.4.10 and Equation 17.4.11) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 17.4.13. The cracks gradually enlarge from 10–50 µm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 17.4.13 to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a *stalactite* that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a *stalagmite*, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 17.4.2).



Figure 17.4.2 Solubility Equilibriums in the Formation of Karst **Landscapes**Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

## Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. Basic oxidesAn oxide that reacts with water to produce a basic solution or dissolves readily in aqueous acid. and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. Acidic oxidesAn oxide that reacts with water to produce an acidic solution or dissolves in aqueous base. or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. As shown in Figure 17.4.3 , there is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. *Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides.* Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

$$Cs_2O_{(s)} + H_2O_{(l)} \rightarrow 2Cs^+_{(aq)} + 2OH^-_{(aq)} \tag{17.4.14}$$

$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)} \tag{17.4.15}$$

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed!

### Note the Pattern

Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete $M^{n+}$ cations and $O^{2-}$ anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is $MoO_3$, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion ($MoO_4^{2-}$):

$$MoO_{3(s)} + 2OH^-_{(aq)} \rightarrow MoO^{2-}_{4(aq)} + H_2O_{(l)} \tag{17.4.16}$$

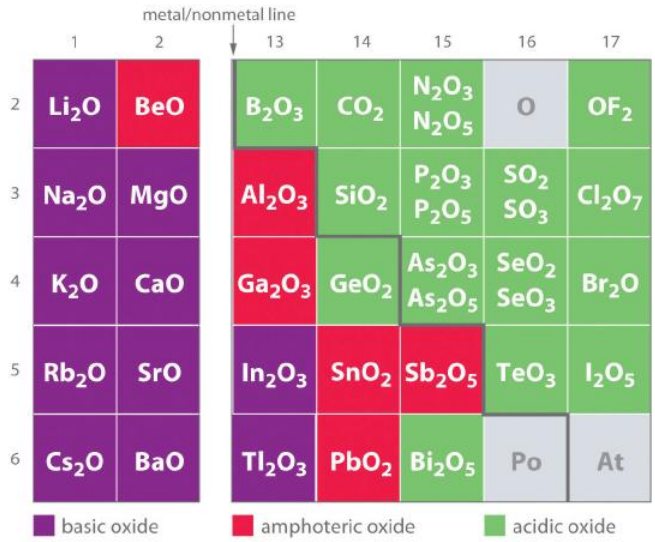



Figure 17.4.3 Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic **Character**There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure 17.4.3, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic *and* basic solutions; consequently, they are called amphoteric oxidesAn oxide that can dissolve in acid to produce water and dissolve in base to produce a soluble complex. (from the Greek *ampho*, meaning "both," as in *amphiprotic*, which was defined in Section 16.1). Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Figure 17.4.4 , for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as $Cr_2O_3{\cdot}3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^-$ ion. The chemical equations for the reactions are as follows:

$$\underset{\text{violet}}{Cr^{3+}(aq)} + 3H_2O(l) \leftarrow Cr(OH)_3(s) + 3H^+(aq) \rightarrow \underset{\text{green}}{[Cr(OH)_4]^-(aq)} + OH^-(aq)$$

**Figure 17.4.4 Chromium(III) Hydroxide [$Cr(OH)_3$ or $Cr_2O_3{\cdot}3H_2O$] Is an Example of an Amphoteric Oxide**All three beakers originally contained a suspension of brownish purple $Cr(OH)_3$(s) (center). When concentrated acid (6 M $H_2SO_4$) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^-$ions.

### Example 17.4.2

Aluminum hydroxide, written as either $Al(OH)_3$ or $Al_2O_3{\cdot}3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

**Given:** amphoteric compound

**Asked for:** dissolution reactions in acid and base

**Strategy:**

Using Equation 17.4.17 and Equation 17.4.18 as a guide, write the dissolution reactions in acid and base solutions.

**Solution:**


https://chem.libretexts.org/@go/page/349764

1. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three $OH^-$ ions per Al, needs three $H^+$ ions:

$$Al(OH)_{3(s)} + 3H^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

   In aqueous solution, $Al^{3+}$ forms the complex ion $[Al(H_2O)_6]^{3+}$.

2. In basic solution, $OH^-$ is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_{3(s)} + OH^-_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)}$$

Exercise

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO{\cdot}H_2O$, is amphoteric. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

**Answer**

$$Cu(OH)_{2(s)} + 2H^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2H_2O_{(l)}$$

$$Cu(OH)_{2(s)} + 2OH^-_{(aq)} \rightarrow [Cu(OH)_4]^{2}_{-(aq)}$$

## Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

### Note the Pattern

The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.

Suppose, for example, we have a solution that contains 1.0 mM $Zn^{2+}$ and 1.0 mM $Cd^{2+}$ and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilibriums can be written as follows:

$$ZnS_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + S^{2-}_{(aq)} \tag{17.4.19a}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{17.4.19b}$$

and

$$CdS_{(s)} \rightleftharpoons Cd^{2+}_{(aq)} + S^{2-}_{(aq)} \tag{17.4.20a}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{17.4.20b}$$

Because the $S^{2-}$ ion is quite basic and reacts extensively with water to give $HS^-$ and $OH^-$, the solubility equilibriums are more accurately written as MS(s) = $M^{2+}$(aq) +$HS^-$(aq) + $OH^{-(aq)}$ rather than MS(s) = $M^{2+}$(aq) +$S2^-$(aq) Here we use the simpler form involving $S^{2-}$, which is justified because we take the reaction of $S^{2-}$ with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{17.4.21a}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{17.4.21b}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{17.4.21c}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{17.4.22a}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{17.4.22b}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{17.4.22c}$$

Thus sulfide concentrations between $1.6 \times 10^{-21}$ M and $8.0 \times 10^{-24}$ M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of $H_2S$ contains 0.10 M $H_2S$ at 20°C. The p$K_{a1}$ for $H_2S$ is 6.97, and p$K_{a2}$ corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:

$$H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^-_{(aq)} \tag{17.4.24a}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{17.4.24b}$$

$$HS^-_{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)} \tag{17.4.24c}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{17.4.24d}$$

We can show that the concentration of $S^{2-}$ is $1.3 \times 10^{-13}$ by comparing $K_{a1}$ and $K_{a2}$ and recognizing that the contribution to $[H^+]$ from the dissociation of $HS^-$ is negligible compared with $[H^+]$ from the dissociation of $H_2S$. Thus substituting 0.10 M in the equation for $K_{a1}$ for the concentration of $H_2S$, which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10\ M} \tag{17.4.5}$$

$$x = 1.1 \times 10^{-4}\ M = [H^+] = [HS^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for $K_{a2}$,

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4}\ M)x}{1.1 \times 10^{-4}\ M} = x = [S^{2-}]$$

Although $[S^{2-}]$ in an $H_2S$ solution is very low ($1.3 \times 10^{-13}$ M), bubbling $H_2S$ through the solution until it is saturated would precipitate both metal ions because the concentration of $S^{2-}$ would then be much greater than $1.6 \times 10^{-21}$ M. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the $H_2S$ solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 17.4.244 to the left. The overall equation for the dissociation of $H_2S$ is as follows:

$$H_2S_{(aq)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)} \tag{17.4.26}$$

Now we can use the equilibrium constant $K$ for the overall reaction, which is the product of $K_{a1}$ and $K_{a2}$, and the concentration of $H_2S$ in a saturated solution to calculate the $H^+$ concentration needed to produce $[S^{2-}]$ of $1.6 \times 10^{-21}$ M:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \tag{17.4.27}$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10\ M)}{1.6 \times 10^{-21}\ M} = 0.88$$

$$[H^+] = 0.94$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in $H^+$ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with $H_2S$.

### Example 17.4.3

A solution contains 0.010 M $Ca^{2+}$ and 0.010 M $La^{3+}$. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3 \cdot 9H_2O$ but not $Ca(C_2O_4) \cdot H_2O$ if the concentration of oxalic acid is 1.0 M? $K_{sp}$ values are $2.32 \times 10^{-9}$ for $Ca(C_2O_4)$ and $2.5 \times 10^{-27}$ for $La_2(C_2O_4)_3$; p$K_{a1}$ = 1.25 and p$K_{a2}$ = 3.81 for oxalic acid.

**Given:** concentrations of cations, $K_{sp}$ values, and concentration and p$K_a$ values for oxalic acid

**Asked for:** concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

**Strategy:**

**A** Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3{\cdot}9H_2O$.

**B** Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the [ox$^{2-}$] needed to precipitate $La_2(C_2O_4)_3{\cdot}9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required [$H^+$].

**Solution:**

**A** Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox$^{2-}$ for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8}$ M and $2.32 \times 10^{-7}$ M.

**B** To prevent $Ca^{2+}$ from precipitating as calcium oxalate, we must add enough $H^+$ to give a maximum oxalate concentration of $2.32 \times 10^{-7}$ M. We can calculate the required [$H^+$] by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H_{(aq)} \rightleftharpoons 2H^+_{(aq)} + C_2O^{2-}_{4(aq)}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7{\times}10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[H^+]^2[ox^{2-}]}{[HO_2CCO_2H]} = \frac{[H^+]^2(2.32 \times 10^{-7})}{1.0}$$

$$[H^+] = 6.1\ M$$

Thus adding enough HCl to give [$H^+$] = 6.1 M will cause only $La_2(C_2O_4)_3{\cdot}9H_2O$ to precipitate from the solution.

Exercise

A solution contains 0.015 M $Fe^{2+}$ and 0.015 M $Pb^{2+}$. What concentration of acid is needed to ensure that $Pb^{2+}$ precipitates as PbS in a saturated solution of $H_2S$, but $Fe^{2+}$ does not precipitate as FeS? $K_{sp}$ values are $6.3 \times 10^{-18}$ for FeS and $8.0 \times 10^{-28}$ for PbS.

**Answer:** 0.018 M $H^+$

## Summary

The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. **Acidic oxides** either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. **Basic oxides** either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called **amphoteric oxides**. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

## Key Takeaway

- The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH.

## Conceptual Problems

1. Which of the following will show the greatest increase in solubility if 1 M $HNO_3$ is used instead of distilled water? Explain your reasoning.
    1. $CuCl_2$
    2. $K[Pb(OH)_3]$
    3. $Ba(CH_3CO_2)_2$
    4. $CaCO_3$
2. Of the compounds $Sn(CH_3CO_2)_2$ and SnS, one is soluble in dilute HCl and the other is soluble only in hot, concentrated HCl. Which is which? Provide a reasonable explanation.
3. Where in the periodic table do you expect to find elements that form basic oxides? Where do you expect to find elements that form acidic oxides?
4. Because water can autoionize, it reacts with oxides either as a base (as $OH^-$) or as an acid (as $H_3O^+$). Do you expect oxides of elements in high oxidation states to be more acidic (reacting with $OH^-$) or more basic (reacting with $H_3O^+$) than the corresponding oxides in low oxidation states? Why?
5. Given solid samples of CrO, $Cr_2O_3$, and $CrO_3$, which would you expect to be the most acidic (reacts most readily with $OH^-$)? Which would be the most basic (reacts most readily with $H_3O^+$)? Why?
6. Which of these elements—Be, B, Al, N, Se, In, Tl, Pb—do you expect to form an amphoteric oxide? Why?

## Numerical Problems

1. A 1.0 L solution contains 1.98 M $Al(NO_3)_3$. What are $[OH^-]$ and $[H^+]$? What pH is required to precipitate the cation as $Al(OH)_3$? $K_{sp} = 1.3 \times 10^{-33}$ and $K_a = 1.05 \times 10^{-5}$ for the hydrated $Al^{3+}$ ion.
2. A 1.0 L solution contains 2.03 M $CoCl_2$. What is $[H^+]$? What pH is required to precipitate the cation as $Co(OH)_2$? $K_{sp} = 5.92 \times 10^{-15}$ and $K_a = 1.26 \times 10^{-9}$ for the hydrated $Co^{2+}$ ion.
3. Given 100 mL of a solution that contains 0.80 mM $Ag^+$ and 0.80 mM $Cu^+$, can the two metals be separated by selective precipitation as the insoluble bromide salts by adding 10 mL of an 8.0 mM solution of KBr? $K_{sp}$ values are $6.27 \times 10^{-9}$ for CuBr and $5.35 \times 10^{-13}$ for AgBr. What maximum $[Br^-]$ will separate the ions?
4. Given 100 mL of a solution that is 1.5 mM in $Tl^+$, $Zn^{2+}$, and $Ni^{2+}$, which ions can be separated from solution by adding 5.0 mL of a 12.0 mM solution of $Na_2C_2O_4$?

| Precipitate | $K_{sp}$ |
|---|---|
| $Tl_2C_2O_4$ | $2 \times 10^{-4}$ |
| $ZnC_2O_4 \cdot 2H_2O$ | $1.38 \times 10^{-9}$ |
| $NiC_2O_4$ | $4 \times 10^{-10}$ |

How many milliliters of 12.0 mM $Na_2C_2O_4$ should be added to separate $Tl^+$ and $Zn^{2+}$ from $Ni^{2+}$?

## Answers

1. $[H^+] = 4.56 \times 10^{-3}$; $[OH^-] = 2.19 \times 10^{-12}$; pH = 2.94
2. 
3. No; both metal ions will precipitate; AgBr will precipitate as $Br^-$ is added, and CuBr will begin to precipitate at $[Br^-] = 8.6 \times 10^{-6}$ M.

4.

## Contributors

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# 17.6: Qualitative Analysis Using Selective Precipitation

**Learning Objectives**

- To know how to separate metal ions by selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using qualitative analysisA procedure for determining the identity of metal ions present in a mixture that does not include information about their amounts., a procedure for discovering the *identity* of metal ions present in the mixture (rather than quantitative information about their amounts).

The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively *less* selective until almost all of the metal ions are precipitated, as illustrated in Figure 17.5.1.

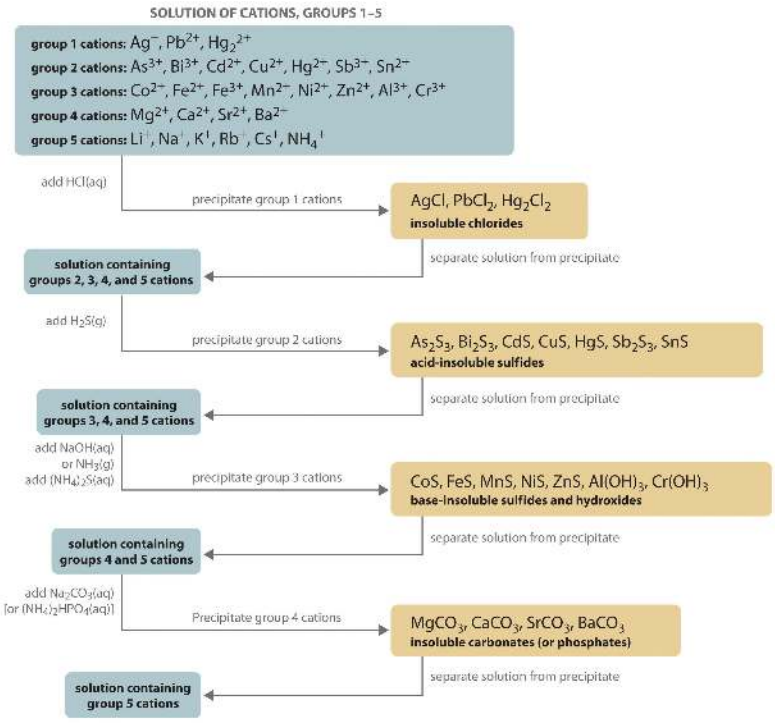



Figure 17.5.1 Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

## Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only $Ag^{+}$, $Pb^{2+}$, and $Hg_2^{2+}$ form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl, $PbCl_2$, and/or $Hg_2Cl_2$ to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

## Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with $H_2S$ gas. Only those metal ions that form very insoluble sulfides, such as $As^{3+}$, $Bi^{3+}$, $Cd^{2+}$, $Cu^{2+}$, $Hg^{2+}$, $Sb^{3+}$, and $Sn^{2+}$, precipitate as their sulfide salts under these acidic conditions. All others, such as $Fe^{2+}$ and $Zn^{2+}$, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

## Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or NaOH is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions $Co^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Ni^{2+}$, and $Zn^{2+}$ precipitate as their sulfides, and the trivalent metal ions $Al^{3+}$ and $Cr^{3+}$ precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains $Fe^{3+}$, sulfide reduces the cation to $Fe^{2+}$, which precipitates as FeS.

## Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When $Na_2CO_3$ is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

## Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals ($Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) and ammonium ($NH_4^+$). We now take a second sample from the *original* solution and add a small amount of NaOH to neutralize the ammonium ion and produce $NH_3$. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. As discussed in Chapter 2, the other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing $Ag^+$, $Pb^{2+}$, and $Hg_2^{2+}$, are all quite insoluble in water. Because $PbCl_2$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $PbCl_2$ present. Isolating the solution and adding a small amount of $Na_2CrO_4$ solution to it will produce a bright yellow precipitate of $PbCrO_4$ if $Pb^{2+}$ was in the original sample (Figure 17.5.2).

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any AgCl because $Ag^+$ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, $Hg_2Cl_2$ *disproportionates* in ammonia ($2Hg_2^{2+} \rightarrow Hg + Hg^{2+}$) to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:



Figure 17.5.2 When a small amount of Na2CrO4 solution is added to a sample containing Pb2+ ions in water, a bright yellow precipitate of PbCrO4 forms. from Wikipedia.

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any AgCl because $Ag^+$ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, $Hg_2Cl_2$ disproportionates in ammonia ($2Hg_2^{2+} \rightarrow Hg + Hg^{2+}$) to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

$$Hg_2Cl_{2(s)} + 2NH_{3(aq)} \rightarrow Hg_{(l)} + Hg(NH_2)Cl_{(s)} + NH_{4(aq)}^+ + Cl_{(aq)}^- \tag{17.39}$$

Any silver ion in the solution is then detected by adding HCl, which reverses the reaction and gives a precipitate of white AgCl that slowly darkens when exposed to light:

$$[Ag(NH_3)_2]_{(aq)}^+ + 2H_{(aq)}^+ + Cl_{(aq)}^- \rightarrow AgCl_{(s)} + 2NH_{4(aq)}^+ \tag{17.40}$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

## Summary

In **qualitative analysis**, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively *less* selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

## Key Takeaway

- Several common metal cations can be identified in a solution using selective precipitation.

## Conceptual Problem

1. Given a solution that contains a mixture of NaCl, $CuCl_2$, and $ZnCl_2$, propose a method for separating the metal ions.

## Contributors

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# CHAPTER OVERVIEW

## 18: Chemical Thermodynamics


18.1: Thermodynamics and Work
18.2: The First Law of Thermodynamics
18.3: The Second Law of Thermodynamics
18.4: Entropy Changes and the Third Law of Thermodynamics
18.5: Free Energy
18.6: Spontaneity and Equilibrium
18.7: Comparing Thermodynamics and Kinetics
18.8: Thermodynamics and Life


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# 18.1: Thermodynamics and Work

**Learning Objectives**

- To understand the relationships between work, heat, and energy.
- To become familiar with the concept of *PV* work.

We begin our discussion of thermodynamics by reviewing some important terms introduced in Chapter 9. First, we need to distinguish between a system and its surroundings. A **system** is that part of the universe in which we are interested, such as a mixture of gases in a glass bulb or a solution of substances in a flask. The **surroundings** are everything else—the rest of the *universe*. We can therefore state the following:

$$system + surroundings = universe \tag{18.1.1}$$

A **closed system**, such as the contents of a sealed jar, cannot exchange matter with its surroundings, whereas an **open system** can; in this case, we can convert a closed system (the jar) to an open system by removing the jar's lid.

In Chapter 9, we also introduced the concept of a state function A property of a system whose magnitude depends on only the present state of the system, not its previous history., a property of a system that depends on only the present state of the system, not its history. Thus a change in a state function depends on only the difference between the initial and final states, not the pathway used to go from one to the other. To help understand the concept of a state function, imagine a person hiking up a mountain (Figure 18.1.1). If the person is well trained and fit, he or she may be able to climb almost vertically to the top (path A), whereas another less athletic person may choose a path that winds gradually to the top (path B). If both hikers start from the same point at the base of the mountain and end up at the same point at the top, their *net change in altitude* will be the same regardless of the path chosen. Hence altitude is a state function. On the other hand, a person may or may not carry a heavy pack and may climb in hot weather or cold. These conditions would influence changes in the hiker's fatigue level, which depends on the path taken and the conditions experienced. Fatigue, therefore, is not a state function. Thermodynamics is generally concerned with state functions and does not deal with how the change between the initial state and final state occurs.




Figure 18.1.1 Altitude Is a State **Function.** When hiking up a mountain, a person may decide to take path A, which is almost vertical, or path B, which gradually winds up to the top. Regardless of the path taken, the net change in altitude going from the initial state (bottom of the climb) to the final state (top of the climb) is the same. Thus altitude is a state function.

## The Connections among Work, Heat, and Energy

The internal energy (*E*)A state function that is the sum of the kinetic and potential energies of all a system's components. of a system is the sum of the potential energy and the kinetic energy of all the components; internal energy is a state function. Although a closed system cannot exchange matter with its surroundings, it can exchange energy with its surroundings in two ways: by doing work or by releasing or absorbing heat—the flow of thermal energy. Work and heat are therefore two distinct ways of changing the internal energy of a system. We defined *work* (*w*) in Chapter 9 as a force *F* acting through a distance *d*:

$w = Fd$

Because work occurs only when an object, such as a person, or a substance, such as water, moves against an opposing force, work requires that a system and its surroundings be connected. In contrast, the flow of *heat*, the transfer of energy due to differences in temperature between two objects, represents a thermal connection between a system and its surroundings. Thus doing work causes a physical displacement, whereas the flow of heat causes a temperature change. The units of work and heat must be the same because both processes result in the transfer of energy. In the SI system, those units are joules (J), the same unit used for energy. There is no difference between an energy change brought about by doing work on a system and an equal energy change brought about by heating it.

The connections among work, heat, and energy were first described by Benjamin Thompson (1753–1814), an American-born scientist who was also known as Count Rumford. While supervising the manufacture of cannons, Rumford recognized the relationship between the amount of work required to drill out a cannon and the temperature of the water used to cool it during the drilling process (Figure 18.1.2). At that time, it was generally thought that heat and work were separate and unrelated phenomena. Hence Rumford's ideas were not widely accepted until many years later, after his findings had been corroborated in other laboratories.

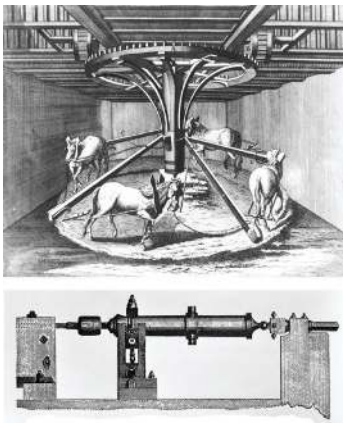


Figure 18.1.2 The Relationship between Heat and **Work** In the 1780s, an American scientist named Benjamin Thompson, also known as Count Rumford, was hired by the Elector of Bavaria to supervise the manufacture of cannons. During the manufacturing process, teams of horses harnessed to a large-toothed wheel supplied the power needed to drill a hole several inches in diameter straight down the center of a solid brass or bronze cylinder, which was cooled by water. Based on his observations, Rumford became convinced that heat and work are equivalent ways of transferring energy.

## *PV* Work

As we saw in Chapter 9, there are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work, focusing on the work done during changes in the pressure or the volume of a gas. To describe this *pressure–volume work* (*PV* work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions.

Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure $P_{int}$ and initial volume $V_i$ (Figure 18.1.3). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston ($P_{ext}$) is less than $P_{int}$, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume ($V_f$) will be greater than $V_i$. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area $A$, the external pressure exerted by the piston is, by definition, the force per unit area: $P_{ext} = F/A$. The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging to give $F = P_{ext}A$ and defining the distance the piston moves ($d$) as $\Delta h$, we can calculate the magnitude of the work performed by the piston by substituting into Equation 18.1.2:

$$w = Fd = P_{ext}A\Delta h \tag{18.1.3}$$



Figure 18.1.3 *PV* **Work** Using a frictionless piston, if the external pressure is less than $P_{int}$ (a), the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume ($V_f$) will be greater than $V_i$. Alternatively, if the external pressure is greater than $P_{int}$ (b), the gas will be compressed, and the surroundings will perform work on the system.

The change in the volume of the cylinder ($\Delta V$) as the piston moves a distance $d$ is $\Delta V = A\Delta h$, as shown in Figure 18.1.4. The work performed is thus

$$w = P_{ext}\Delta V \tag{18.1.4}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m$^2$) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)\Delta V = \frac{newton}{m^2 \times m^3}$$

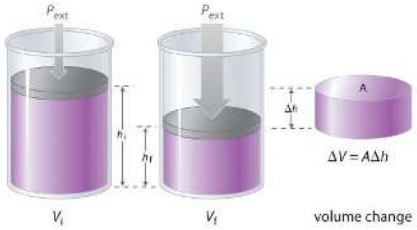



Figure 18.1.4 Work Performed with a Change in Volume The change in the volume ($\Delta V$) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by $w = P_{ext}\Delta V$.

If we use atmospheres for $P$ and liters for $V$, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant $R$:

$$R = \frac{0.08206\ L \cdot atm}{mol \cdot K} = \frac{8.314\ J}{mol \cdot K}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J. (For more information on the ideal gas law, see Chapter 10.)

Whether work is defined as having a positive sign or a negative sign is a matter of convention. In Chapter 9, we defined heat flow *from* a system *to* its surroundings as negative. Using that same sign convention, we define work done *by* a system *on* its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings.This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done *on* the surroundings than in the work done *by* the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 18.4 must be written with a negative sign to describe *PV* work done *by* the system as negative:

$w = P_{ext}\Delta V$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done *by* a system *on* its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done *on* a system *by* its surroundings.

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, *PV* work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

In contrast to internal energy, work is not a state function. We can see this by examining Figure 18.1.5, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume

remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from ($V_1$, $P_1$) to ($V_2$, $P_2$), which means that work is not a state function.

### Note the Pattern

Internal energy is a state function, whereas work is not.

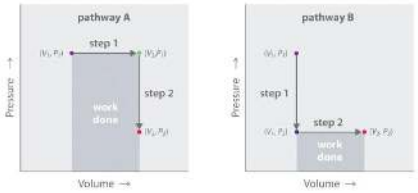



Figure 18.1.5 Work Is Not a State **Function**In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although ($V_1$, $P_1$) and ($V_2$, $P_2$) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken.

### Example 18.1.1

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

**Given:** final volume, compression ratio, and external pressure

**Asked for:** work done

**Strategy:**

**A** Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio.

**B** Use Equation 18.1.5 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

**Solution:**

**A** To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: $V_f$ = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is $V_i$ = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$w = -P_{ext}\Delta V = -\left(40.0\ atm\right)\left(0.400\ L - 0.0400\ L\right) = 14.4\ L \cdot atm$$

Converting from liter-atmospheres to joules,

$$w = -P_{ext}\Delta V = -\left(14.4\ \cancel{L \cdot atm}\right)\left[101.3 J/\left(\cancel{L \cdot atm}\right)\right] = -1.46 \times 10^3\ J$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm. How much work in liter-atmospheres and joules was required to take a single breath? During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath. How much additional work in joules did he require to take a breath while exercising?

**Answer:** −0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

## Summary

**Thermodynamics** is the study of the interrelationships among heat, work, and the energy content of a system at equilibrium. The sum of the potential energy and the kinetic energy of all the components of a system is the **internal energy (*E*)** of the system, which is a **state function**. When the pressure or the volume of a gas is changed, any mechanical work done is called *PV work*. Work done by a system on its surroundings is given a negative value, whereas work done on a system by its surroundings has a positive value.

## Key Takeaway

- Internal energy is a state function that is the sum of the potential and kinetic energy of the system, whereas work is not a state function.

## Key Equation

**Definition of *PV* work**

Equation 18.1.5: $w = -P_{ext}\Delta V$

## Conceptual Problems

1. Thermodynamics focuses on the energetics of the reactants and products and provides information about the composition of the reaction system at equilibrium. What information on reaction systems is not provided by thermodynamics?
2. Given a system in which a substance can produce either of two possible products, A → B or A → C, which of the following can be predicted using chemical thermodynamics?
    1. At equilibrium, the concentration of product C is greater than the concentration of product B.
    2. Product C forms more quickly than product B.
    3. The reaction A → C is exothermic.
    4. Low-energy intermediates are formed in the reaction A → B.
    5. The reaction A → C is spontaneous.
3. In what two ways can a closed system exchange energy with its surroundings? Are these two processes path dependent or path independent?
4. A microwave oven operates by providing enough energy to rotate water molecules, which produces heat. Can the change in the internal energy of a cup of water heated in a microwave oven be described as a state function? Can the heat produced be described as a state function?

## Answers

1. Thermodynamics tells us nothing about the rate at which reactants are converted to products.
2. 
3. heat and work; path dependent
4. 

## Numerical Problems

1. Calculate the work done in joules in each process.
    1. compressing 12.8 L of hydrogen gas at an external pressure of 1.00 atm to 8.4 L at a constant temperature
    2. expanding 21.9 L of oxygen gas at an external pressure of 0.71 atm to 23.7 L at a constant temperature
2. How much work in joules is done when oxygen is compressed from a volume of 22.8 L and an external pressure of 1.20 atm to 12.0 L at a constant temperature? Was work done by the system or the surroundings?
3. Champagne is bottled at a $CO_2$ pressure of about 5 atm. What is the force on the cork if its cross-sectional area is 2.0 $cm^2$? How much work is done if a 2.0 g cork flies a distance of 8.2 ft straight into the air when the cork is popped? Was work done by the system or the surroundings?

4. One mole of water is converted to steam at 1.00 atm pressure and 100°C. Assuming ideal behavior, what is the change in volume when the water is converted from a liquid to a gas? If this transformation took place in a cylinder with a piston, how much work could be done by vaporizing the water at 1.00 atm? Is work done by the system or the surroundings?
5. Acceleration due to gravity on the earth's surface is 9.8 $m/s^2$. How much work is done by a 175 lb person going over Niagara Falls (approximately 520 ft high) in a barrel that weighs 145 lb?
6. Recall that force can be expressed as mass times acceleration ($F = ma$). Acceleration due to gravity on the earth's surface is 9.8 $m/s^2$.
    1. What is the gravitational force on a person who weighs 52 kg?
    2. How much work is done if the person leaps from a burning building out of a window that is 20 m above the ground?
    3. If the person lands on a large rescue cushion fitted with a pressure-release valve that maintains an internal pressure of 1.5 atm, how much air is forced out of the cushion?
7. A gas is allowed to expand from a volume of 2.3 L to a volume of 5.8 L. During the process, 460 J of heat is transferred from the surroundings to the gas.
    1. How much work has been done if the gas expands against a vacuum?
    2. How much work has been done if the gas expands against a pressure of 1.3 atm?
    3. What is the change in the internal energy of the system?
8. One mole of an ideal gas is allowed to expand from an initial volume of 0.62 L to a final volume of 1.00 L at constant temperature against a constant external pressure of 1.0 atm. How much work has been done?

## Answers

1.
2.
3.
4.
5. −230 kJ
6.
7. 1. 0 J
    2. −460 J
    3. 0 J
8.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 18.2: The First Law of Thermodynamics

**Learning Objectives**

- To calculate changes in internal energy.

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamicsThe energy of the universe is constant: $\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0$., which states that the *energy of the universe is constant*. Using Equation 18.1.1, we can express this law mathematically as follows:

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$

$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the $CO_2/H_2O$ product mixture is less than that of the isooctane/$O_2$ reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred ($q$) and the work done ($w$):

$$\Delta E_{sys} = q + w$$

Although $q$ and $w$ are not state functions on their own, their sum ($\Delta E_{sys}$) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed, as discussed in Section 18.5. Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

### Note the Pattern

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

### Note the Pattern

Although $q$ and $w$ are not state functions, their sum ($\Delta E_{sys}$) is independent of the path taken and therefore is a state function.

### Example 18.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy ($\Delta E$) of the gas in joules?

**Given:** initial volume, final volume, external pressure, and quantity of energy transferred as heat

**Asked for:** total change in internal energy

**Strategy:**

**A** Determine the sign of $q$ to use in Equation 18.2.2.

**B** From Equation 18.1.5, calculate $w$ from the values given. Substitute this value into Equation 18.2.2 to calculate $\Delta E$.

**Solution:**

**A** From Equation 18.2.2, we know that $\Delta E = q + w$. We are given the magnitude of $q$ (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, $q$ is negative by convention.

**B** Because the gas is being compressed, we know that work is being done *on* the system, so $w$ must be positive. From Equation 18.1.5,

$$w = -P_{ext}\Delta V = -\left(8.0\ \cancel{atm}\right)\left(0.0500\ \cancel{L} - 0.400\ \cancel{L}\right)\left(\frac{101.3\ J}{\cancel{L}\cdot\cancel{atm}}\right) = 284\ J$$

Thus

$$\Delta E = q + w = -140\ J + 284\ J = 144\ J$$

In this case, although work is done *on* the gas, increasing its internal energy, heat flows *from* the system *to* the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy ($\Delta E$) of the gas in joules?

**Answer:** −216 J

### Note the Pattern

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

## Enthalpy

To further understand the relationship between heat flow ($q$) and the resulting change in internal energy ($\Delta E$), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that $PV$ work is the only kind of work possible for the system, so we can substitute its definition from Equation 18.1.5 into Equation 18.7 to obtain the following:

$$\Delta E = q - p\Delta V$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and $\Delta V$ is zero. Under these conditions, the heat flow (often given the symbol $q_v$ to indicate constant volume) must equal $\Delta E$:

$$\underset{constant\ volume}{q_v = \Delta E}$$

No $PV$ work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol $q_p$ to indicate constant pressure. Replacing $q$ in Equation 18.2.3 by $q_p$ and rearranging to solve for $q_p$,

$$\underset{constant\ pressure}{q_p = \Delta E + P\Delta V}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the $PV$ work done, as we stated in Chapter 9.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (*H*)A state function that is the sum of the system's internal energy E and the product of its pressure P and volume V. H=E+PV is defined as $H = E + PV$. At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta E + \Delta (PV) = \Delta E + P\Delta (V)$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy in Section Section 9.1, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

### Note the Pattern

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$.

### Example 18.2.2

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate Δ*H* and Δ*E* for the melting of ice at 0.0°C. (For more information on enthalpy, see Section 9.2.)

**Given:** enthalpy of fusion for ice, pressure, and molar volumes of ice and water

**Asked for:** Δ*H* and Δ*E* for ice melting at 0.0°C

**Strategy:**

**A** Determine the sign of *q* and set this value equal to Δ*H*.

**B** Calculate Δ(*PV*) from the information given.

**C** Determine Δ*E* by substituting the calculated values into Equation 18.2.6.

**Solution:**

**A** Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, $q$ = +6.01 kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H$ = 6.01 kJ.

**B** To find Δ*E* using Equation 18.2.6, we need to calculate Δ(*PV*). The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta PV = P\Delta V = P\left(V_f - V\right) = (1.00\ atm)\,(0.0180\ L - 0.0197\ lL)$$

$$= \left(-1.7 \times 10{-}3\ \cancel{L \cdot atm}\right)\left(101.3\ J/\cancel{L \cdot atm}\right)$$

**C** Substituting the calculated values of Δ*H* and *P*Δ*V* into Equation 18.2.6,

$$\Delta E = \Delta H - P\Delta V = -6010\ J - (-0.0017\ J) = 6010\ J = 6.01\ kJ$$

Exercise

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate Δ*H* and Δ*E* for the conversion of C (graphite) to C (diamond) under these conditions.

**Answer:** Δ*H* = 1.85 kJ/mol; Δ*E* = 1.85 kJ/mol

## The Relationship between Δ*H* and Δ*E*

If Δ*H* for a reaction is known, we can use the change in the enthalpy of the system (Equation 18.2.6) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (Δ*V* = 0). Under these conditions, we can simplify Equation 18.2.6 to Δ*H* = Δ*E*. If gases are involved, however, Δ*H* and Δ*E* can differ significantly. We can calculate Δ*E* from the measured value of Δ*H* by using the right side of Equation 18.11 together with the ideal gas law, *PV* = *nRT*. Recognizing that Δ(*PV*) = Δ(*nRT*), we can rewrite Equation 18.2.6 as follows:

$$\Delta H = \Delta E + \Delta (PV) = \Delta E + \Delta (nRT)$$

At constant temperature, Δ(*nRT*) = *RT*Δ*n*, where Δ*n* is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta E = \Delta H - RT\Delta n$$

For reactions that result in a net production of gas, $\Delta n > 0$, so $\Delta E < \Delta H$. Conversely, endothermic reactions ($\Delta H > 0$) that result in a net consumption of gas have $\Delta n < 0$ and $\Delta E > \Delta H$. The relationship between $\Delta H$ and $\Delta E$ for systems involving gases is illustrated in Example 4.

### Note the Pattern

For reactions that result in a net production of gas, $\Delta E < \Delta H$. For endothermic reactions that result in a net consumption of gas, $\Delta E > \Delta H$.

### Example 18.2.3

The combustion of graphite to produce carbon dioxide is described by the equation C (graphite, s) + $O_2$(g) → $CO_2$(g). At 298 K and 1.0 atm, $\Delta H$ = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is $\Delta E$ for the reaction?

**Given:** balanced chemical equation, temperature, pressure, $\Delta H$, and molar volume of reactant

**Asked for:** $\Delta E$

**Strategy:**

**A** Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

**B** Substitute this value and the data given into Equation 18.2.8 to obtain $\Delta E$.

**Solution:**

**A** In this reaction, 1 mol of gas ($CO_2$) is produced, and 1 mol of gas ($O_2$) is consumed. Thus $\Delta n = 1 - 1 = 0$.

**B** Substituting this calculated value and the given values into Equation 18.2.8,

$$\Delta E = \Delta H - RT\Delta n = (-393.5\ kJ/mol) - [8.314\ J/mol \cdot K]\,(298\ K)\,(0)$$

$$= (-393.5\ kJ/mol) - (0\ J/mol) = -393.5\ kJ$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise

Calculate $\Delta E$ for the conversion of oxygen gas to ozone at 298 K: 3$O_2$(g) → 2$O_3$(g). The value of $\Delta H$ for the reaction is 285.4 kJ.

**Answer:** 288 kJ

As the exercise in Example 4 illustrates, the magnitudes of $\Delta H$ and $\Delta E$ for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

### Summary

The **first law of thermodynamics** states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow ($q$) and internal energy ($E$) are related to the system's **enthalpy ($H$)**. The heat flow is equal to the change in the internal energy of the system plus the $PV$ work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for $\Delta E$.

### Key Takeaway

- Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the $PV$ work done.

## Key Equations

**Internal energy change**

Equation 18.2.2: $\Delta E_{sys} = q + w$

**Enthalpy change**

Equation 18.2.6: $\Delta H = \Delta E + \Delta(PV)$

**Relationship between Δ *H* and Δ *E* for an ideal gas**

Equation 18.2.8: $\Delta E = \Delta H - RT\Delta n$

## Conceptual Problems

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.
2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of *q* and *w*.
3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?
4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.
    1. What is the sign of the enthalpy change for this reaction?
    2. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the molar enthalpy change?
    3. Propose an explanation for the decrease in temperature.
5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?
6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?
7. The *enthalpy of combustion* ($\Delta H_{comb}$) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g) \rightarrow CO_2(g) + H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of $\Delta H_{comb}$. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.
    1. cyclopropane or cyclopentane
    2. butane or 2-methylpropane
    3. hexane or cyclohexane
8. Using a structural argument, explain why the *trans* isomer of 2-butene is more stable than the *cis* isomer. The enthalpies of formation of *cis*- and *trans*-2-butene are −7.1 kJ/mol and −11.4 kJ/mol, respectively.
9. Using structural arguments, explain why cyclopropane has a positive $\Delta H_f°$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H_f°$ (−18.4 kJ/mol). (Hint: consider bond angles.)

## Answers

1.
2.
3. At constant pressure, $\Delta H = \Delta E + P\Delta V$.
4.
5.
6.
7.

8.

9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.

## Numerical Problems

1. A block of $CO_2$ weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of $CO_2$ is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of $CO_2$ under these conditions?

2. Zinc and HCl react according to the following equation:

   $Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$

   When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of *q* and *w*, and what is the change in internal energy?

3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:

   $$2C_2H_2\,(g) + 5O_2\,(g) \rightarrow 4CO_2\,(g) + 2H_2O\,(l)\;\;\;\; \Delta H=-2599\;kJ$$

   Calculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of $O_2$ at 1.0 atm at 20°C. What is the change in internal energy for the reaction?

4. When iron dissolves in 1.00 M aqueous HCl, the products are $FeCl_2$(aq) and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

## Answer

1. −350 J; 8.2 kJ
2.
3.
4.

## Contributors

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Modified by Joshua B. Halpern

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# 18.3: The Second Law of Thermodynamics

**Learning Objectives**

- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy ($U$). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as $NH_4NO_3$, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 18.3.1.

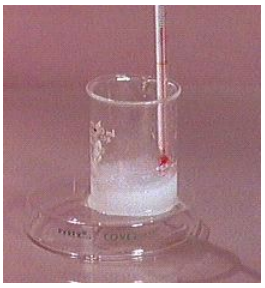


Figure 18.3.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "disorder". In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

## Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure 18.3.2. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately $10^{68}$ different ways they might be arranged, which corresponds to $10^{68}$ different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

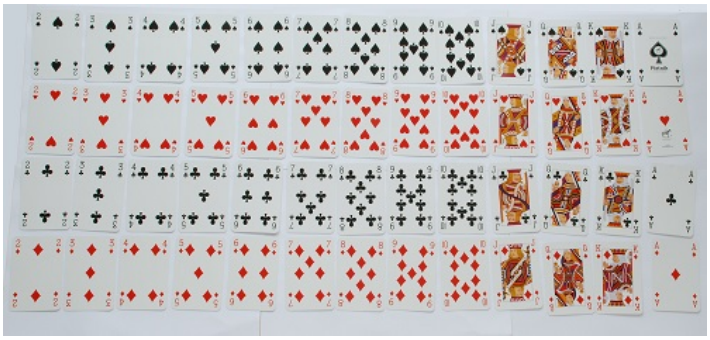


Figure 18.3.2: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately $10^{68}$ different arrangements, which correspond to $10^{68}$ different microstates. (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure 18.3.3). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure 18.3.3, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the most probable arrangement. The others are not impossible but simply less likely.

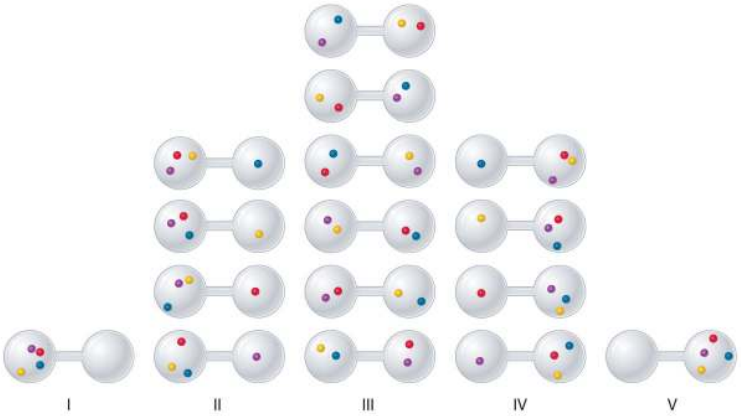



Figure 18.3.3: The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume

There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains $2.69 \times 10^{22}$ molecules ($6.022 \times 10^{23}$ molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all $2.69 \times 10^{22}$ molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

> Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of $\Delta S_{vap}$ is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of $\Delta S_{vap}$. For instance, $\Delta S_{vap}$ for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 18.3.4, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved $Na^+$ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the $Cl^-$ ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors.

In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

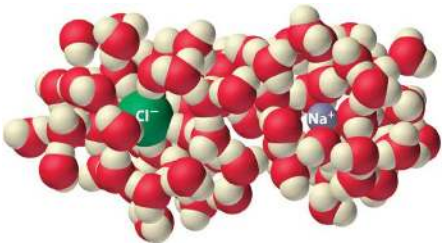



Figure 18.3.4: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

### ✔ Example 18.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

**Given**: amounts of substances and temperature

**Asked for**: higher entropy

**Strategy**:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

**Solution**:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of $NH_3$ molecules. With four atoms instead of one, the $NH_3$ molecules have more motions available, leading to a greater number of microstates. Hence we predict that the $NH_3$ sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

### ? Exercise 18.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

**Answer a**

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

**Answer a**

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

**Video Solution**

## Reversible and Irreversible Changes

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = - P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, $\Delta U = q + w$. Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{18.3.1}$$

> Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process ($q_{rev}$) to define entropy quantitatively.

## The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred ($q_{rev}$) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \quad \text{and} \quad \Delta S = \frac{q_{\text{rev}}}{T} \tag{18.3.2}$$

Because the numerator ($q_{rev}$) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 18.3.1 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{18.3.3}$$

$$= T\Delta S - P\Delta V \tag{18.3.4}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the $PV$ work done.

To illustrate the use of Equation 18.3.2 and Equation 18.3.4, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its $T$ constant (Figure 18.3.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, ΔV > 0, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0. \tag{18.3.5}$$

According to Equation 18.3.4, this means that $q_{rev}$ must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}. \tag{18.3.6}$$

The corresponding change in entropy of the universe is then as follows:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \\ &= 0\end{aligned}$$

Thus no change in $\Delta S_{univ}$ has occurred.

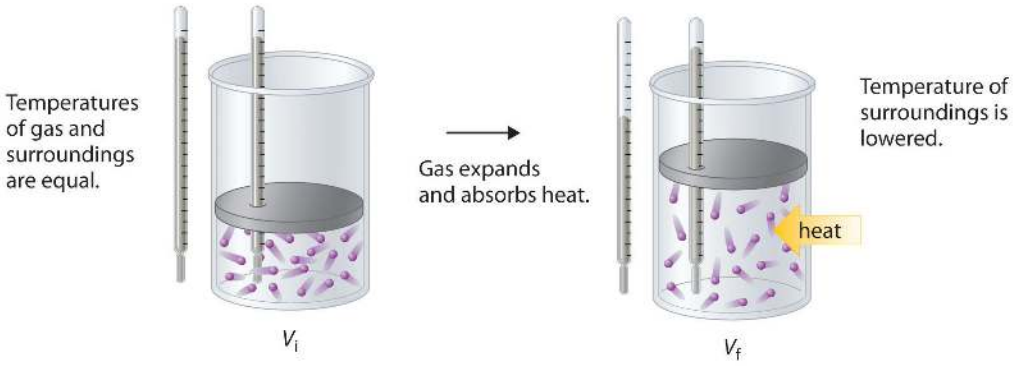



Figure 18.3.5: Expansion of Gas at Constant Temperature

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 18.3.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 18.3.2, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

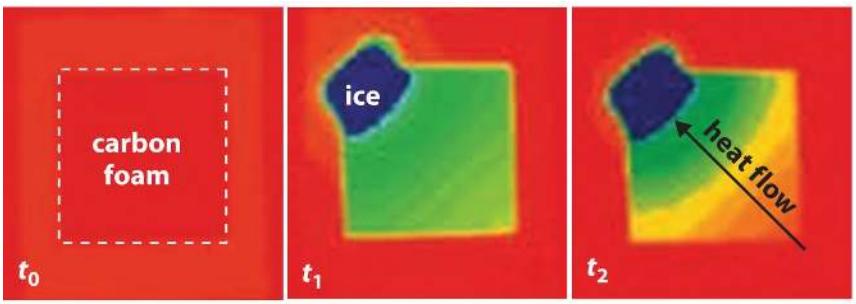



Figure 18.3.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

In this case, $\Delta S_{fus}$ = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol•K) = $\Delta S_{sys}$. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = −(6.01 kJ/mol)/(273 K) = −22.0 J/(mol•K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0\ J/(mol•K) - 22.0\ J/(mol•K) = 0$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

### The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where $T_{cold}$ and $T_{hot}$ are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{univ} = \Delta S_{cold} + \Delta S_{hot} = \frac{q}{T_{cold}} + \left(-\frac{q}{T_{hot}}\right) \tag{18.3.7}$$

The numerators on the right side of Equation 18.3.7 are the same in magnitude but opposite in sign. Whether $\Delta S_{univ}$ is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than $q/T_{cold}$, and $\Delta S_{univ}$ must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which $\Delta S_{univ}$ is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which $\Delta S_{univ}$ is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 18.3.7).



Figure 18.3.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

### Example 18.3.2: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to have plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and may have disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with $\Delta H = -2.1$ kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

**Given**: ΔH and temperature

**Asked for:** ΔS and relative degree of order

**Strategy**:

Use Equation 18.3.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

**Solution**

a. We know from Equation 18.3.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where $q_{rev}$ = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol}\cdot\text{K)}$$

b. The fact that ΔS < 0 means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.




**Video** 18.3.1**:** *Time lapse tin pest reaction.*

*Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C)*

## ? Exercise 18.3.2

Elemental sulfur exists in two forms: an orthorhombic form ($S_\alpha$), which is stable below 95.3°C, and a monoclinic form ($S_\beta$), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—$S_\alpha$ or $S_\beta$?

**Answer a**

1.09 J/(mol•K)

**Answer b**

$S_\alpha$

## Summary

For a given system, the greater the number of microstates, the higher the entropy. During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{18.3.8}$$

A measure of the disorder of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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# 18.4: Entropy Changes and the Third Law of Thermodynamics

**Learning Objectives**

- To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 18.4.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

**Third Law of Thermodynamics**

The entropy of any perfectly ordered, crystalline substance at absolute zero is *zero*.

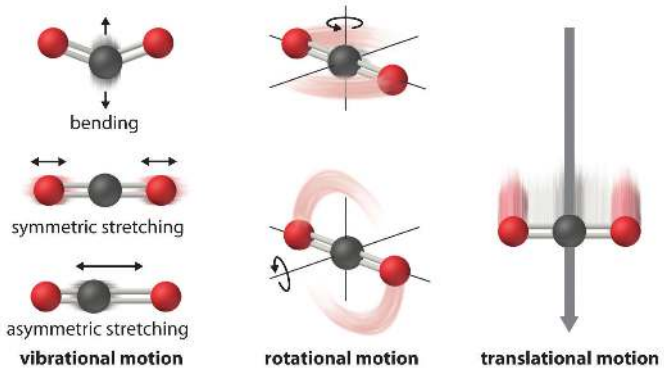



Figure 18.4.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity ($C_p$) as a function of temperature and then plotting the quantity $C_p/T$ versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

## Calculating ΔS from Standard Molar Entropy Values

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to S = 0 J/(mol•K)] and 298 K.

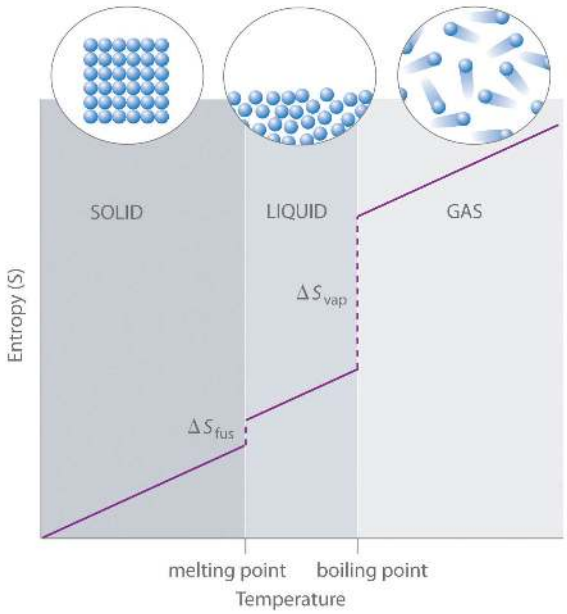



Figure 18.4.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid ($\Delta S_{fus}$). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas ($\Delta S_{vap}$).

As shown in Table 18.4.1, for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol•K), whereas S° for water vapor is 188.8 J/(mol•K). Likewise, S° is 260.7 J/(mol•K) for gaseous $I_2$ and 116.1 J/(mol•K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 18.4.2, which is a generalized plot of the entropy of a substance versus temperature.

Table 18.4.1: Standard Molar Entropy Values of Selected Substances at 25°C

| **Gases** | | **Liquids** | | **Solids** | |
|---|---|---|---|---|---|
| *Substance* | *S° [J/(mol•K)]* | *Substance* | *S° [J/(mol•K)]* | *Substance* | *S° [J/(mol•K)]* |
| He | 126.2 | $H_2O$ | 70.0 | C (diamond) | 2.4 |
| $H_2$ | 130.7 | $CH_3OH$ | 126.8 | C (graphite) | 5.7 |
| Ne | 146.3 | $Br_2$ | 152.2 | LiF | 35.7 |
| Ar | 154.8 | $CH_3CH_2OH$ | 160.7 | $SiO_2$ (quartz) | 41.5 |
| Kr | 164.1 | $C_6H_6$ | 173.4 | Ca | 41.6 |
| Xe | 169.7 | $CH_3COCl$ | 200.8 | Na | 51.3 |
| $H_2O$ | 188.8 | $C_6H_{12}$ (cyclohexane) | 204.4 | $MgF_2$ | 57.2 |
| $N_2$ | 191.6 | $C_8H_{18}$ (isooctane) | 329.3 | K | 64.7 |
| $O_2$ | 205.2 | | | NaCl | 72.1 |
| $CO_2$ | 213.8 | | | KCl | 82.6 |
| $I_2$ | 260.7 | | | $I_2$ | 116.1 |


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**Note**

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table 18.4.1 also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol•K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol•K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.

**Note**

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 18.4.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane ($C_8H_{18}$; 2,2,4-trimethylpentane).

**Example 18.4.1**

Use the data in Table 18.4.1 to calculate ΔS° for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

**Given**: standard molar entropies, reactants, and products

**Asked for**: ΔS°

**Strategy**:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 18.4.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

**Solution**:

The balanced chemical equation for the complete combustion of isooctane ($C_8H_{18}$) is as follows:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(g)$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\Delta S^\circ_{rxn} = \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \tag{18.4.1}$$

$$= [8S^\circ(CO_2) + 9S^\circ(H_2O)] - [S^\circ(C_8H_{18}) + \frac{25}{2}S^\circ(O_2)] \tag{18.4.2}$$

$$= \{[8 \text{ mol } CO_2 \times 213.8 \text{ J/(mol} \cdot \text{K)}] + [9 \text{ mol } H_2O \times 188.8 \text{ J/(mol} \cdot \text{K)}]\} \tag{18.4.3}$$

$$- \left\{[1 \text{ mol } C_8H_{18} \times 329.3 \text{ J/(mol} \cdot \text{K)}] \right. \tag{18.4.4}$$

$$\left. + \left[\frac{25}{2} \text{ mol } O_2 \times 205.2 \text{ J/(mol} \cdot \text{K)}\right]\right\}$$

$$= 515.3 \text{ J/K} \tag{18.4.5}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

**? Exercise 18.4.1**

Use the data in Table 18.4.1 to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene ($C_6H_6$) to give cyclohexane ($C_6H_{12}$).

**Answer**: −361.1 J/K

## Calculating ΔS from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned previously, the molar heat capacity ($C_p$) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure. Similarly, $C_v$ is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature in Figure 18.4.2 is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow ($q_{rev}$) by $\Delta S = q_{rev}/T$. Because $q_{rev} = nC_p\Delta T$ at constant pressure or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes from $T_1$ to $T_2$ is as follows:

$$\Delta S = \frac{q_{\text{rev}}}{T} = nC_{\text{p}}\frac{\Delta T}{T} \quad \text{(constant pressure)} \tag{18.4.6}$$

As you will discover in more advanced math courses than is required here, it can be shown that this is equal to the following:For a review of natural logarithms, see Essential Skills 6 in Chapter 11.

$$\Delta S = nC_{\text{p}} \ln \frac{T_2}{T_1} \quad \text{(constant pressure)} \tag{18.20}$$

Similarly,

$$DeltaS = nC_{\text{v}} \ln \frac{T_2}{T_1} \quad \text{(constant volume)} \tag{18.21}$$

Thus we can use a combination of heat capacity measurements (Equation 18.20 or Equation 18.21) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 18.18) to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure 18.4.3): an orthorhombic form with a highly ordered structure ($S_\alpha$) and a less-ordered monoclinic form ($S_\beta$). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from $S_\alpha$ to $S_\beta$ can be described by the thermodynamic cycle shown in part (b) in Figure 18.4.3, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to $S_\beta$ ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, $\Delta S_3$ can be calculated from the overall entropy change ($\Delta S_t$) for the $S_\alpha$–$S_\beta$ transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of $S_\alpha$ and $S_\beta$, $\Delta H_{fus(\alpha)}$, and the melting point of $S_\alpha$.)

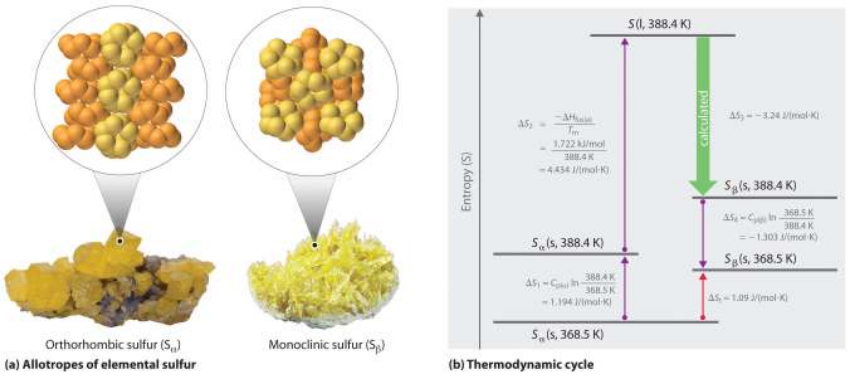



Figure 18.4.3: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other(a) Orthorhombic sulfur ($S_\alpha$) has a highly ordered structure in which the $S_8$ rings are stacked in a "crankshaft" arrangement. Monoclinic sulfur ($S_\beta$) is also composed of $S_8$ rings but has a less-ordered structure. (b) At 368.5 K, $S_\alpha$ undergoes a phase transition to $S_\beta$. Although $\Delta S_3$ cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of $S_\alpha$ ($T_m$ = 115.2°C = 388.4 K) and $\Delta S_t$ for the overall phase transition [calculated to be 1.09 J/(mol•K) in the exercise in Example 6], we can calculate $\Delta S_3$ from the values given in part (b) in Figure 18.4.3 where $C_{p(\alpha)}$ = 22.70 J/mol•K and $C_{p(\beta)}$ = 24.77 J/mol•K (subscripts on ΔS refer to steps in the cycle):

$$\Delta S_t = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \tag{18.4.7}$$

$$1.09\ \text{J/(mol}\cdot\text{K)} = C_{p(\alpha)} \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{fus}}{T_m} + \Delta S_3 + C_{p(\beta)} \ln\left(\frac{T_4}{T_3}\right) \tag{18.4.8}$$

$$= 22.70\ \text{J/(mol}\cdot\text{K)} \ln\left(\frac{388.4}{368.5}\right) + \left(\frac{1.722\ \text{kJ/mol}}{388.4\ \text{K}} \times 1000\ \text{J/kJ}\right) \tag{18.4.9}$$

$$+ \Delta S_3 + 24.77\ \text{J/(mol}\cdot\text{K)} \ln\left(\frac{368.5}{388.4}\right) \tag{18.4.10}$$

$$= [1.194\ \text{J/(mol}\cdot\text{K)}] + [4.434\ \text{J/(mol}\cdot\text{K)}] + \Delta S_3 + [-1.303\ \text{J/(mol}\cdot\text{K)}] \tag{18.4.11}$$

Solving for $\Delta S_3$ gives a value of −3.24 J/(mol•K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), $\Delta S_3$ is negative.

## Summary

- Entropy changes can be calculated using the "products minus reactants" rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

The third law of thermodynamics states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the absolute entropy of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard temperature of 298 K is its standard molar entropy (S°). We can use the "products minus reactants" rule to calculate the standard entropy change (ΔS°) for a reaction using tabulated values of S° for the reactants and the products.

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# 18.5: Free Energy

**Learning Objectives**

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of $\Delta S_{univ}$ is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using $\Delta S_{univ}$ requires that we calculate $\Delta S$ for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

## Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy ($G$), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{18.5.1}$$

Because it is a combination of state functions, $G$ is also a state function.

**J. Willard Gibbs (1839–1903)**

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on ($\Delta G$), the change in $G$, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as $G$. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{18.5.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 18.5.2 to $\Delta G = q - q_{rev}$. Thus $\Delta G$ is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if $\Delta G$ is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of $\Delta G$ for a system determines the direction in which change is spontaneous, we can rewrite the relationship between $\Delta S$ and $q_{rev}$, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T} \tag{18.5.3}$$

with the definition of $\Delta H$ in terms of $q_{rev}$

$$q_{rev} = \Delta H \tag{18.5.4}$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{18.5.5}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{18.5.6}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{18.5.7}$$

Multiplying both sides of the inequality by −T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{18.5.8}$$

which is equal to $\Delta G$ (Equation 18.5.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 18.5.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of $\Delta H_{vap}$ (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 18.5.5), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1091\ \text{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate $\Delta G$ for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ C} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1088\ \text{J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ C} = 1090\ \text{J} = -\Delta G_{90^\circ C}$, as we would predict.

### Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 18.5.2), setting $\Delta G = 0$, and solving for $T$,

$$0\ \text{J} = 40{,}657\ \text{J} - T(108.96\ \text{J/K})$$
$$T = 373.15\ \text{K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, $\Delta G$ is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, $\Delta G$ is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 18.5.1 shows how the $\Delta H$ and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

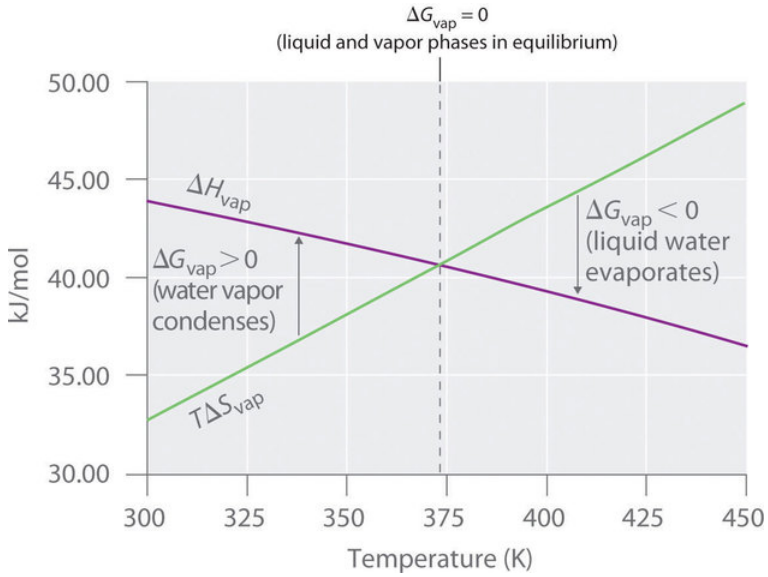



Figure 18.5.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

## The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 18.5.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{18.5.9}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 18.5.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 18.5.1: Approximate Thermodynamic Efficiencies of Various Devices

| Device | Energy Conversion | Approximate Efficiency (%) |
|---|---|---|
| large electrical generator | mechanical → electrical | 99 |
| chemical battery | chemical → electrical | 90 |
| home furnace | chemical → heat | 65 |
| small electric tool | electrical → mechanical | 60 |
| space shuttle engine | chemical → mechanical | 50 |
| mammalian liver cell | chemical → chemical | 30–50 |
| spinach leaf cell | light → chemical | 30 |
| internal combustion engine | chemical → mechanical | 25–30 |
| fluorescent light | electrical → light | 20 |
| solar cell | light → electricity | 10-20 |
| incandescent light bulb | electricity → light | 5 |
| yeast cell | chemical → chemical | 2–4 |

## Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their

standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 18.5.10:

$$\Delta G°= \Delta H°-T\Delta S° \tag{18.5.10}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

A positive ΔG° means that the equilibrium constant is less than 1.

**Example 18.5.1**

Calculate the standard free-energy change ($\Delta G^o$) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°($H_2O_2$) = 109.6 J/(mol•K),
- S°($O_2$) = 205.2 J/(mol•K), and
- S°($H_2$) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

**Given**: balanced chemical equation, ΔH° and S° for reactants and products

**Asked for:** spontaneity of reaction as written

**Strategy**:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 18.5.10, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

**Solution**

A To calculate ΔG° for the reaction, we need to know $\Delta H^o$, $\Delta S^o$, and $T$. We are given $\Delta H^o$, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\text{ mol }\mathrm{H_2O_2} \times 109.6\text{ J/(mol}\cdot\mathrm{K})] \\ &\quad - \{[1\text{ mol }\mathrm{H_2} \times 130.7\text{ J/(mol}\cdot\mathrm{K})] + [1\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\mathrm{K})]\} \\ &= -226.3\text{ J/K (per mole of }\mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, $\Delta S^o$ is very negative for this reaction.

B Substituting the appropriate quantities into Equation 18.5.10,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\text{ kJ/mol} - (298.15\text{ K})[-226.3\text{ J/(mol}\cdot\mathrm{K}) \times 1\text{ kJ/1000 J}] \\ &= -187.78\text{ kJ/mol} + 67.47\text{ kJ/mol} \\ &= -120.31\text{ kJ/mol}\end{aligned}$$

The negative value of $\Delta G^o$ indicates that the reaction is spontaneous as written. Because $\Delta S^o$ and $\Delta H^o$ for this reaction have the same sign, the sign of $\Delta G^o$ depends on the relative magnitudes of the $\Delta H^o$ and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable $\Delta S^o$ term and for the energy needed to break bonds in the reactants.

**Exercise 18.5.1**

Calculate the standard free-energy change ($\Delta G^o$) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

**Hint**

At 25°C, the standard enthalpy change ($\Delta H^o$) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°($N_2H_4$) = 121.2 J/(mol•K),
- S°($N_2$) = 191.6 J/(mol•K), and
- S°($H_2$) = 130.7 J/(mol•K).

**Answer**

149.5 kJ/mol

no, not spontaneous

Video Solution

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation ($\Delta G_f^\circ$)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of $Cl_2$ gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation ($\Delta H^\circ_f$) and the standard entropy of formation ($\Delta S^\circ_f$) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{18.5.11}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{18.5.12}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

**The "Products minus Reactants" Rule**

The $\Delta G^o$ of a reaction can be calculated from tabulated $\Delta G^\circ_f$ values (Table T1) using the “products minus reactants” rule.

**Example 18.5.2**

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- $\Delta G^\circ_f$(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol. Is the reaction spontaneous as written?

**Given**: balanced chemical equation and values of $\Delta G^\circ_f$ for isooctane, $CO_2$, and $H_2O$

**Asked for**: spontaneity of reaction as written

**Strategy**:

Use the "products minus reactants" rule to obtain $\Delta G^\circ_{rxn}$, remembering that $\Delta G^\circ_f$ for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

**Solution**

The balanced chemical equation for the reaction is as follows:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(l)$$

We are given $\Delta G^\circ_f$ values for all the products and reactants except $O_2$(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f\,(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(CO_2) + 9\Delta G^\circ_f(H_2O)] - \left[1\Delta G^\circ_f(C_8H_{18}) + \frac{25}{2}\Delta G^\circ_f(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the $\Delta G^\circ_f$ of the stable products: water and carbon dioxide.

## ? Exercise 18.5.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- $\Delta G^\circ_f$(benzene) = 124.5 kJ/mol
- $\Delta G^\circ_f$ (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

**Answer**

92.8 kJ; no

Video Solution

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither $\Delta H$ nor $\Delta S$ vary greatly with temperature.

## ✓ Example 18.5.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),

- S°($NH_3$) = 192.8 J/(mol•K), and
- $\Delta H^\circ_f$ ($NH_3$) = −45.9 kJ/mol.

**Given**: balanced chemical equation, temperatures, S° values, and $\Delta H^\circ_f$ for $NH_3$

**Asked for**: ΔG° and ΔG at 300°C

**Strategy**:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that $\Delta H^\circ_f$ for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 18.5.10 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 18.5.2 to obtain ΔG for the reaction at 300°C.

**Solution**

A To calculate ΔG° for the reaction using Equation 18.5.10, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)] \\ &= [2 \text{ mol } NH_3 \times 192.8 \text{ J/(mol} \cdot \text{K)}] \\ &\quad - \{[1 \text{ mol } N_2 \times 191.6 \text{ J/(mol} \cdot \text{K)}] + [3 \text{ mol } H_2 \times 130.7 \text{ J/(mol} \cdot \text{K)}]\} \\ &= -198.1 \text{ J/K (per mole of } N_2) \end{aligned} \tag{18.5.13}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of $\Delta H^\circ_f$ ($NH_3$) is given, and $\Delta H^\circ_f$ is zero for both $N_2$ and $H_2$:

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\Delta H^\circ_f(NH_3) - [\Delta H^\circ_f(N_2) + 3\Delta H^\circ_f(H_2)] \\ &= [2 \times (-45.9 \text{ kJ/mol})] - [(1 \times 0 \text{ kJ/mol}) + (3 \times 0 \text{ kJ/mol})] \\ &= -91.8 \text{ kJ(per mole of } N_2)\end{aligned}$$

B Inserting the appropriate values into Equation 18.5.10

$$\begin{aligned}\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ &= (-91.8 \text{ kJ}) - (298 \text{ K})(-198.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -32.7 \text{ kJ (per mole of } N_2)\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 18.5.2:

$$\begin{aligned}\Delta G_{300°C} &= \Delta H_{300°C} - (573 \text{ K})(\Delta S_{300°C}) \\ &= \Delta H^\circ - (573 \text{ K})\Delta S^\circ \\ &= (-91.8 \text{ kJ}) - (573 \text{ K})(-198.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) \\ &= 21.7 \text{ kJ (per mole of } N_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its $K_{eq}$ is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

**? Exercise 18.5.3**

Calculate

a. $\Delta G^\circ$ and
b. $\Delta G_{750°C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that $\Delta H$ and $\Delta S$ do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°($O_2$) = 205.2 J/(mol•K),
- S°($NO_2$) = 240.1 J/(mol•K),
- $\Delta H^\circ_f$($NO_2$) = 33.2 kJ/mol, and
- $\Delta H^\circ_f$ (NO) = 91.3 kJ/mol.

**Answer a**

−72.5 kJ/mol of $O_2$

**Answer b**

33.8 kJ/mol of $O_2$

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 18.5.10, as illustrated in Example 18.5.4.

## Example 18.5.4

As you saw in Example 18.5.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

**Given**: ΔH° and ΔS°

**Asked for**: temperature at which reaction changes from spontaneous to nonspontaneous

**Strategy**:

Set ΔG° equal to zero in Equation 18.5.10 and solve for T, the temperature at which the reaction becomes nonspontaneous.

**Solution**

In Example 18.5.3, we calculated that ΔH° is −91.8 kJ/mol of $N_2$ and ΔS° is −198.1 J/K per mole of $N_2$, corresponding to ΔG° = −32.7 kJ/mol of $N_2$ at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 18.5.10 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

## Exercise 18.5.4

As you found in the exercise in Example 18.5.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

**Answer**

792.6 K

Video Solution

## Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change:

$$\Delta G° = \Delta H° - T\Delta S°$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation ($\Delta G^\circ_f$), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

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# 18.6: Spontaneity and Equilibrium

**Learning Objectives**

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously: $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient $Q$ versus the equilibrium constant $K$. (For more information on the reaction quotient and the equilibrium constant, see Chapter 15.) Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 18.6.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes. Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. The relationship between $\Delta S_{univ}$ and $\Delta G_{sys}$ was described in Section 18.5. In this section, we explore the relationship between the standard free energy of reaction ($\Delta G°$) and the equilibrium constant ($K$).

**Table 18.6.1 Criteria for the Spontaneity of a Process as Written**

| Spontaneous | Equilibrium | Nonspontaneous* |
|---|---|---|
| $\Delta S_{univ} > 0$ | $\Delta S_{univ} = 0$ | $\Delta S_{univ} < 0$ |
| $\Delta G_{sys} < 0$ | $\Delta G_{sys} = 0$ | $\Delta G_{sys} > 0$ |
| $Q < K$ | $Q = K$ | $Q > K$ |
| *Spontaneous in the *reverse* direction. | | |

## Free Energy and the Equilibrium Constant

Because $\Delta H°$ and $\Delta S°$ determine the magnitude of $\Delta G°$ (Equation 18.5.5), and because $K$ is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express $K$ in terms of $\Delta G°$ and vice versa. As you learned in Section 18.5, $\Delta G$ is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating $\Delta H$ from the equation for $\Delta G$. Using higher math, the general relationship can be shown as follows:

$$\Delta G = V\Delta P - S\Delta T$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 18.29 simplifies to

$$\Delta G = V\Delta P$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important. What Equation 18.6.2 tells us is how the free energy changes as the pressure changes at constant temperature.

Assuming ideal gas behavior, we can replace the $V$ in Equation 18.6.2 by $nRT/P$ (where $n$ is the number of moles of gas and $R$ is the ideal gas constant) and express $\Delta G$ in terms of the initial and final pressures ($P_i$ and $P_f$, respectively) as in Equation 18.4.1.

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRTln\left(\frac{P_f}{P_i}\right)$$

To actually show the final step one has to consider infinitesmal changes in both the free energy and the pressure and then integrate both sides of the equation using calculus, which is beyond the scope of this course. If the initial state is the standard state with $P_i$ = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure $P$ can be written as follows:

$$G - G^o = nRTln\ P$$

This can be rearranged as follows:

$$G = G^o + nRTln\ P$$

As you will soon discover, Equation 18.6.5 allows us to relate $\Delta G°$ and $K_p$. Any relationship that is true for $K_p$ must also be true for $K$ because $K_p$ and $K$ are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for $\Delta G$:

$$\Delta G = \sum mG_{products} - \sum mG_{reactants} = (cG_C + dG_D) - (aG_A + bG_B)$$

Substituting Equation 18.6.5 for each term into Equation 18.6.7,

$$\Delta G = [(cG_C + cRTln\ P_C) + (dG_D + dRTln\ P_D)] - [(aG_A + aRTln\ P_A) + (bG_B + bRTln\ P_B)]$$

Combining terms gives the following relationship between $\Delta G$ and the reaction quotient $Q$:

$$\Delta G = \Delta G^o + RTln\left(\frac{P_C^c P_D^d}{P_A^a P_B^b}\right) = \Delta G^o + RTln\ Q$$

where $\Delta G°$ indicates that all reactants and products are in their standard states. In Chapter 15, you learned that for gases $Q = K_p$ at equilibrium, and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between $\Delta G°$ and $K_p$ for gases as follows:

$$0 = \Delta G^o + RTln\ K_P$$

$$\Delta G^o = -RTln\ K_P$$

If the products and reactants are in their standard states and $\Delta G° < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G° > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

### Note the Pattern

For a spontaneous process under standard conditions, $K_{eq}$ and $K_p$ are greater than 1.

### Example 18.6.1

In Example 18.5.3, we calculated that $\Delta G° = -32.7$ kJ/mol of $N_2$ for the reaction $N_2(g)+3H_2(g \rightleftharpoons 2NH_3(g)$ This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate $\Delta G$ for the same reaction under the following nonstandard conditions: $P(N_2) = 2.00$ atm, $P(H_2) = 7.00$ atm, $P(NH_3) = 0.021$ atm, and $T = 100°C$. Does the reaction favor products or reactants?

**Given:** balanced chemical equation, partial pressure of each species, temperature, and $\Delta G°$

**Asked for:** whether products or reactants are favored

**Strategy:**

**A** Using the values given and Equation 18.6.8, calculate $Q$.

**B** Substitute the values of $\Delta G°$ and $Q$ into Equation 18.6.8 to obtain $\Delta G$ for the reaction under nonstandard conditions.

**Solution:**

**A** The relationship between $\Delta G°$ and $\Delta G$ under nonstandard conditions is given in Equation 18.6.8. Substituting the partial pressures given, we can calculate $Q$:

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.021)^2}{(2.00)\,(7.00)^3} = 6.4 \times 10^{-7}$$

**B** Substituting the values of $\Delta G°$ and $Q$ into Equation 18.6.8,

$$\Delta G = \Delta G^o + RTln\ Q = -32.7\ kJ + \left[\left(8.314\ \cancel{J}/\cancel{K}\right)\left(373\ \cancel{K}\right)\left(1\ kJ/1000\ \cancel{kJ}\right) ln\left(6.4 \times 10^{-7}\right)\right]$$

$$= -32.7\ kJ + (-44\ kJ) = -77\ kJ/mol\ N_2$$

Because $\Delta G < 0$ and $Q < 1.0$, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise

Calculate $\Delta G$ for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: $T$ = 50°C, $P(NO)$ = 0.0100 atm, $P(O_2)$ = 0.200 atm, and $P(NO_2)$ = 1.00 × $10^{-4}$ atm. The value of $\Delta G°$ for this reaction is −72.5 kJ/mol of $O_2$. Are products or reactants favored?

**Answer:** −92.9 kJ/mol of $O_2$; the reaction is spontaneous to the right as written, so products are favored.

### Example 18.6.2

Calculate $K_p$ for the reaction of $H_2$ with $N_2$ to give $NH_3$ at 25°C. As calculated in Example 18.5.3 , $\Delta G°$ for this reaction is −32.7 kJ/mol of $N_2$.

**Given:** balanced chemical equation from Example 10, $\Delta G°$, and temperature

**Asked for:** $K_p$

**Strategy:**

Substitute values for $\Delta G°$ and $T$ (in kelvins) into Equation 18.6.9 to calculate $K_p$, the equilibrium constant for the formation of ammonia.

**Solution:**

In Example 18.5.3 , we used tabulated values of ΔG° to calculate $\Delta G°$ for this reaction (−32.7 kJ/mol of $N_2$). For equilibrium conditions, rearranging Equation 18.6.9,

$$\Delta G^o = -RTln\ K_P$$

$$\frac{-\Delta G^o}{RT} = ln\ K_P$$

Inserting the value of $\Delta G°$ and the temperature (25°C = 298 K) into this equation,

$$ln\ K_P = -\frac{\left(-32.7\ \cancel{kJ}\right)\left(1000\ \cancel{J}/\cancel{kJ}\right)}{8.314\ \cancel{J}/\cancel{K}\left(298\ \cancel{K}\right)} = 13.2$$

$$K_P = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. As we saw in Chapter 15, however, the *rate* at which the reaction occurs at room temperature is too slow to be useful.

Exercise

Calculate $K_p$ for the reaction of NO with $O_2$ to give $NO_2$ at 25°C. As calculated in the exercise in Example 10, $\Delta G°$ for this reaction is −70.5 kJ/mol of $O_2$.

**Answer:** $2.2 \times 10^{12}$

Although $K_p$ is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant $K$ is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of $K_p$ and $K$ in Chapter 15 and showed that they are related:

$$K_P = K\,(RT)^{\Delta n}$$

where $\Delta n$ is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 18.36 can be written in a more general form:

$$\Delta G^o = -RTln\ K$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 18.38 for the difference between $K_p$ and $K$.Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of activities or fugacities in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 18.26 and Equation 18.6.11 provides insight into how the components of $\Delta G°$ influence the magnitude of the equilibrium constant:

$$\Delta G^o = \Delta H^o - T\Delta S^o = -RTln\ K$$

Notice that $K$ becomes larger as $\Delta S°$ becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, $K$ increases as $\Delta H°$ decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

### Note the Pattern

The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.

## Temperature Dependence of the Equilibrium Constant

The fact that $\Delta G°$ and $K$ are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 18.6.12, which can be rearranged as follows:

$$ln\ K = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Assuming $\Delta H°$ and $\Delta S°$ are temperature independent, for an exothermic reaction ($\Delta H° < 0$), the magnitude of $K$ decreases with increasing temperature, whereas for an endothermic reaction ($\Delta H° > 0$), the magnitude of $K$ increases with increasing temperature. The quantitative relationship expressed in Equation 18.6.13 agrees with the qualitative predictions made by applying Le Chatelier's principle, which we discussed in Chapter 15. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of $K$. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of $K$. Equation 18.6.13 also shows that the *magnitude* of $\Delta H°$ dictates how rapidly $K$ changes as a function of temperature. In contrast, the magnitude and sign of $\Delta S°$ affect the magnitude of $K$ but not its temperature dependence.

If we know the value of $K$ at a given temperature and the value of $\Delta H°$ for a reaction, we can estimate the value of $K$ at any other temperature, even in the absence of information on $\Delta S°$. Suppose, for example, that $K_1$ and $K_2$ are the equilibrium constants for a reaction at temperatures $T_1$ and $T_2$, respectively. Applying Equation 18.6.13 gives the following relationship at each temperature:

$$ln\ K_1 = \frac{\Delta H^o}{RT_1} + \frac{\Delta S^o}{R}$$
$$ln\ K_2 = \frac{\Delta H^o}{RT_2} + \frac{\Delta S^o}{R}$$

Subtracting ln $K_1$ from ln $K_2$,

$$ln\ K_2 - ln\ K_1 = ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Thus calculating $\Delta H°$ from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature ($K_1$) allow us to calculate the value of the equilibrium constant at any other temperature ($K_2$), assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature.

### Example 18.6.3

The equilibrium constant for the formation of $NH_3$ from $H_2$ and $N_2$ at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 13. What is $K_p$ at 500°C? (Use the data from Example 10.)

**Given:** balanced chemical equation, $\Delta H°$, initial and final $T$, and $K_p$ at 25°C

**Asked for:** $K_p$ at 500°C

**Strategy:**

Convert the initial and final temperatures to kelvins. Then substitute appropriate values into Equation 18.41 to obtain $K_2$, the equilibrium constant at the final temperature.

**Solution:**

The value of $\Delta H°$ for the reaction obtained using Hess's law is −91.8 kJ/mol of $N_2$. If we set $T_1$ = 25°C = 298.K and $T_2$ = 500°C = 773 K, then from Equation 18.6.13 we obtain the following:

$$= \frac{\left(-91.8 \cancel{kJ}\right)\left(1000 \cancel{J}/\cancel{kJ}\right)}{8.314 \cancel{J}/\cancel{K}} \left(\frac{1}{298 \cancel{K}} - \frac{1}{773 \cancel{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \pm \times 10^{-10}$$

$$K_2 = \left(5.4 \times 10^5\right)\left(1.3 \pm \times 10^{-10}\right) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise

In the exercise in Example 13, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with $O_2$ to give $NO_2$ at 25°C. Use the $\Delta H_f°$ values in the exercise in Example 10 to calculate $K_p$ for this reaction at 1000°C.

**Answer:** $5.6 \times 10^{-4}$

## Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express $\Delta G$ in terms of the partial pressures of the reactants and products, which gives us a relationship between $\Delta G$ and $K_p$, the equilibrium constant of a reaction involving gases, or $K$, the equilibrium constant expressed in terms of concentrations. If $\Delta G° < 0$, then $K$ or $K_p > 1$, and products are favored over reactants. If $\Delta G° > 0$, then $K$ or $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then $K$ or $K_p = 1$, and the system is at equilibrium. We can use the measured equilibrium constant $K$ at one temperature and $\Delta H°$ to estimate the equilibrium constant for a reaction at any other temperature.

## Key Takeaway

- The change in free energy of a reaction can be expressed in terms of the standard free-energy change and the equilibrium constant $K$ or $K_p$ and indicates whether a reaction will occur spontaneously under a given set of conditions.

## Key Equations

**Relationship between standard free-energy change and equilibrium constant**

Equation 18.6.9: $\Delta G^o = -RT ln\ K$

**Temperature dependence of equilibrium constant**

Equation 18.6.11: $ln\ K = \frac{-\Delta H^o}{RT} + \frac{-\Delta S^o}{R}$

**Calculation of $K$ at second temperature**

Equation 18.6.11: $ln\ \frac{K_2}{K_1} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

## Conceptual Problems

1. Do you expect products or reactants to dominate at equilibrium in a reaction for which $\Delta G°$ is equal to
    1. 1.4 kJ/mol?
    2. 105 kJ/mol?
    3. −34 kJ/mol?

2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?
3. What happens to the change in free energy of the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$ if the pressure is increased while the temperature remains constant? if the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?
4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

## Numerical Problems

1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form $CO_2$ and $H_2$, as shown in the equation $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$, for which $\Delta H° = -41.0$ kJ/mol and $\Delta S° = -42.3$ J cal/(mol·K) at 25°C and 1 atm.
    1. What is $\Delta G°$ for this reaction?
    2. What is $\Delta G$ if the gases have the following partial pressures: $P(CO) = 1.3$ atm, $P(H_2O) = 0.8$ atm, $P(CO_2) = 2.0$ atm, and $P(H_2) = 1.3$ atm?
    3. What is $\Delta G$ if the temperature is increased to 150°C assuming no change in pressure?
2. Methane and water react to form carbon monoxide and hydrogen according to the equation $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
    1. What is the standard free energy change for this reaction?
    2. What is $K_p$ for this reaction?
    3. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?
    4. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?
    5. At what temperature does the reaction become spontaneous?
3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.
    1. $CCl_4(g) + 6\ H_2O(l) \rightleftharpoons CO_2(g) + 4HCl(aq)$; $\Delta G° = -377$ kJ/mol
    2. $Xe(g) + 2F_2(g) \rightleftharpoons XeF_4(s)$; $\Delta H° = -66.3$ kJ/mol, $\Delta S° = -102.3$ J/(mol·K)
    3. $PCl_3(g) + S \rightleftharpoons PSCl_3(l)$; $\Delta G_f°(PCl_3) = -272.4$ kJ/mol, $\Delta G_f°(PSCl_3) = -363.2$ kJ/mol
4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.
    1. $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$; $\Delta G° = -225.8$ kJ/mol
    2. $CoCl2(s) + 6\ H_2O(l) \rightleftharpoons 6CoCl_2 \cdot 6\ H_2O(s)$; $\Delta H_{rxn}° = -352$ kJ/mol, $\Delta S_{rxn}° = -899$ J/(mol·K)
    3. $PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$; $(PCl_3)$; $\Delta G_f°(PCl_3) = -272.4$ kJ/mol, $\Delta G_f°(POCl_3) = -558.5$ kJ/mol
5. The gas-phase decomposition of $N_2O_4$ to $NO_2$ is an equilibrium reaction with $K_p = 4.66 \times 10^{-3}$. Calculate the standard free-energy change for the equilibrium reaction between $N_2O_4$ and $NO_2$.
6. The standard free-energy change for the dissolution $K_4Fe(CN)_6 \cdot H_2O(s) \rightleftharpoons 4K^+(aq) + Fe(CN)_6^{4-}(aq) + H_2O(l)$ is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?
7. Ammonia reacts with water in liquid ammonia solution (am) according to the equation $NH_3(g) + H_2O(am) \rightleftharpoons NH_4^+(am) + OH^-(am)$ The change in enthalpy for this reaction is 21 kJ/mol, and $\Delta S° = -303$ J/(mol·K). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (−31°C)?
8. At 25°C, a saturated solution of barium carbonate is found to have a concentration of $[Ba^{2+}] = [CO_3^{2-}] = 5.08 \times 10^{-5}$ M. Determine $\Delta G°$ for the dissolution of $BaCO_3$.
9. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions is $Pb_3(PO_4)_2(s) + 4H^+(aq) \rightleftharpoons 3Pb^{2+}(aq) + 2H_2PO_4^-(aq)$ for which $\log K = -1.80$. What is $\Delta G°$ for this reaction?
10. The conversion of butane to 2-methylpropane is an equilibrium process with $\Delta H° = -2.05$ kcal/mol and $\Delta G° = -0.89$ kcal/mol.

1. What is the change in entropy for this conversion?
2. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?
3. What is the equilibrium constant for this reaction?

11. The reaction of $CaCO_3(s)$ to produce $CaO(s)$ and $CO_2(g)$ has an equilibrium constant at 25°C of $2 \times 10^{-23}$. Values of $\Delta H_f°$ are as follows: $CaCO_3$, −1207.6 kJ/mol; CaO, −634.9 kJ/mol; and $CO_2$, −393.5 kJ/mol.
    1. What is $\Delta G°$ for this reaction?
    2. What is the equilibrium constant at 900°C?
    3. What is the partial pressure of $CO_2(g)$ in equilibrium with CaO and $CaCO_3$ at this temperature?
    4. Are reactants or products favored at the lower temperature? at the higher temperature?
12. In acidic soils, dissolved $Al^{3+}$ undergoes a complex formation reaction with $SO_4^{2-}$ to form $[AlSO_4^+]$. The equilibrium constant at 25°C for the reaction $Al^{3+}(aq) + SO_4^{2-}(aq) \rightleftharpoons AlSO_4^+(aq)$ is 1585.
    1. What is $\Delta G°$ for this reaction?
    2. How does this value compare with $\Delta G°$ for the reaction $Al^{3+}(aq) + F^-(aq) \rightleftharpoons AlF^{2+}(aq)$ for which $K = 10^7$ at 25°C?
    3. Which is the better ligand to use to trap $Al^{3+}$ from the soil?

## Answers

1. 1. −28.4 kJ/mol
    2. −26.1 kJ/mol
    3. −19.9 kJ/mol
2. 
3. 1. $1.21 \times 10^{66}$; equilibrium lies far to the right.
    2. $1.89 \times 10^{6}$; equilibrium lies to the right.
    3. $5.28 \times 10^{16}$; equilibrium lies far to the right.
4. 
5. 13.3 kJ/mol
6. 
7. $5.1 \times 10^{-21}$
8. 
9. 10.3 kJ/mol
10. 
11. 1. 129.5 kJ/mol
    2. 6
    3. 6.0 atm
    4. Products are favored at high *T*; reactants are favored at low *T*.
12. 

## Contributors

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# 18.7: Comparing Thermodynamics and Kinetics

**Learning Objectives**

- To understand the differences between the information that thermodynamics and kinetics provide about a system.

Because thermodynamics deals with state functions, it can be used to describe the overall properties, behavior, and equilibrium composition of a system. It is not concerned with the particular pathway by which physical or chemical changes occur, however, so it cannot address the rate at which a particular process will occur. Although thermodynamics provides a significant constraint on what can occur during a reaction process, it does not describe the detailed steps of what actually occurs on an atomic or a molecular level.

| Note |
| --- |
| Thermodynamics focuses on the energetics of the products and the reactants, whereas kinetics focuses on the pathway from reactants to products. |

Table 18.4 gives the numerical values of the equilibrium constant (K) that correspond to various approximate values of ΔG°. Note that ΔG° ≥ +10 kJ/mol or ΔG° ≤ −10 kJ/mol ensures that an equilibrium lies essentially all the way to the left or to the right, respectively, under standard conditions, corresponding to a reactant-to-product ratio of approximately 10,000:1 (or vice versa). Only if ΔG° is quite small (±10 kJ/mol) are significant amounts of both products and reactants present at equilibrium. Most reactions that we encounter have equilibrium constants substantially greater or less than 1, with the equilibrium strongly favoring either products or reactants. In many cases, we will encounter reactions that are strongly favored by thermodynamics but do not occur at a measurable rate. In contrast, we may encounter reactions that are not thermodynamically favored under standard conditions but nonetheless do occur under certain nonstandard conditions.

**Table 18.4** The Relationship between K and ΔG° at 25°C

| ΔG° (kJ/mol) | K | Physical Significance |
| --- | --- | --- |
| 500 | $3 \times 10^{-88}$ | For all intents and purposes, the reaction does not proceed in the forward direction: only reactants are present at equilibrium. |
| 100 | $3 \times 10^{-18}$ | |
| 10 | $2 \times 10^{-2}$ | Both forward and reverse reactions occur: significant amounts of both products and reactants are present at equilibrium. |
| 0 | 1 | |
| −10 | 60 | |
| −100 | $3 \times 10^{17}$ | For all intents and purposes, the forward reaction proceeds to completion: only products are present at equilibrium. |
| −500 | $4 \times 10^{87}$ | |

A typical challenge in industrial processes is a reaction that has a large negative value of ΔG° and hence a large value of K but that is too slow to be practically useful. In such cases, mixing the reactants results in only a physical mixture, not a chemical reaction. An example is the reaction of carbon tetrachloride with water to produce carbon dioxide and hydrochloric acid, for which ΔG° is −232 kJ/mol:

$$CCl_4(l) + 2H_2O(l) \rightleftharpoons CO_2(g) + 2HCl(g) \tag{18.42}$$

The value of K for this reaction is $5 \times 10^{40}$ at 25°C, yet when $CCl_4$ and water are shaken vigorously at 25°C, nothing happens: the two immiscible liquids form separate layers, with the denser $CCl_4$ on the bottom. In comparison, the analogous reaction of $SiCl_4$ with water to give $SiO_2$ and HCl, which has a similarly large equilibrium constant, occurs almost explosively. Although the two reactions have comparable thermodynamics, they have very different kinetics!

There are also many reactions for which ΔG° << 0 but that do not occur as written because another possible reaction occurs more rapidly. For example, consider the reaction of lead sulfide with hydrogen peroxide. One possible reaction is as follows:

$$PbS(s) + 4H_2O_2(l) \rightleftharpoons PbO2(s) + SO_2(g) + 4H_2O(l) \tag{18.43}$$

for which ΔG° is −886 kJ/mol and K is $10^{161}$. Yet when lead sulfide is mixed with hydrogen peroxide, the ensuing vigorous reaction does not produce $PbO_2$ and $SO_2$. Instead, the reaction that actually occurs is as follows:

$$PbS(s) + 4H_2O_2(l) \rightleftharpoons PbSO_4(s) + 4H_2O(l) \tag{18.7.1}$$

This reaction has a ΔG° value of −1181 kJ/mol, within the same order of magnitude as the reaction in Equation 18.43, but it occurs much more rapidly.

Now consider reactions with ΔG° > 0. Thermodynamically, such reactions do not occur spontaneously under standard conditions. Nonetheless, these reactions can be made to occur under nonstandard conditions. An example is the reduction of chromium(III) chloride by hydrogen gas:

$$\mathrm{CrCl_3(s)} + \frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{CrCl_2(s)} + \mathrm{HCl(g)}$$

At 25°C, ΔG° = 35 kJ/mol and $K_p = 7 \times 10^{-7}$. However, at 730°C, ΔG° = −52 kJ/mol and $K_p = 5 \times 10^2$; at this elevated temperature, the reaction is a convenient way of preparing chromium(II) chloride in the laboratory. Moreover, removing HCl gas from the system drives the reaction to completion, as predicted by Le Chatelier's principle. Although the reaction is not thermodynamically spontaneous under standard conditions, it becomes spontaneous under nonstandard conditions.

There are also cases in which a compound whose formation appears to be thermodynamically prohibited can be prepared using a different reaction. The reaction for the preparation of chlorine monoxide from its component elements, for example, is as follows:

$$\frac{1}{2}\mathrm{O_2(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)}$$

for which $\Delta G^\circ_f$ is 97.9 kJ/mol. The large positive value of $\Delta G^\circ_f$ for this reaction indicates that mixtures of chlorine and oxygen do not react to any extent to form $Cl_2O$. Nonetheless, $Cl_2O$ is easily prepared using the reaction

$$\mathrm{HgO(s)} + 2\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{HgCl_2(s)}$$

which has a ΔG° of −22.2 kJ/mol and a $K_p$ of approximately $1 \times 10^4$.

Finally, the ΔG° values for some reactions are so positive that the only way to make them proceed in the desired direction is to supply external energy, often in the form of electricity. Consider, for example, the formation of metallic lithium from molten lithium chloride:

$$\mathrm{LiCl(l)} \rightleftharpoons \mathrm{Li(l)} + \frac{1}{2}\mathrm{Cl_2(g)}$$

Even at 1000°C, ΔG is very positive (324 kJ/mol), and there is no obvious way to obtain lithium metal using a different reaction. Hence in the industrial preparation of metallic lithium, electrical energy is used to drive the reaction to the right.

> **Note**
>
> A reaction that does not occur under standard conditions can be made to occur under nonstandard conditions, such as by driving the reaction to completion using Le Chatelier's principle or by providing external energy.

Often reactions that are not thermodynamically spontaneous under standard conditions can be made to occur spontaneously if coupled, or connected, in some way to another reaction for which ΔG° << 0. Because the overall value of ΔG° for a series of reactions is the sum of the ΔG° values for the individual reactions, virtually any unfavorable reaction can be made to occur by chemically coupling it to a sufficiently favorable reaction or reactions. In the preparation of chlorine monoxide from mercuric oxide and chlorine (Equation 18.47), we have already encountered one example of this phenomenon of coupled reactions, although we did not describe it as such at the time. We can see how the chemical coupling works if we write Equation 18.47 as the sum of three separate reactions:

$$\frac{1}{2}O_2(g) + Cl_2(g) \rightleftharpoons Cl_2O(g) \qquad \Delta G^\circ = 97.9\ \text{kJ/mol} \tag{1}$$

$$HgO(s) \rightleftharpoons Hg(l) + \frac{1}{2}O_2(g) \qquad \Delta G^\circ = 58.5\ \text{kJ/mol} \tag{2}$$

$$Hg(l) + Cl_2(g) \rightleftharpoons HgCl_2(s) \qquad \Delta G^\circ = -178.6\ \text{kJ/mol} \tag{3}$$

$$HgO(s) + 2Cl_2(g) \rightleftharpoons Cl_2O(g) + HgCl_2(s) \qquad \Delta G^\circ_{rxn} = -22.2\ \text{kJ/mol} \tag{18.7.2}$$

Comparing the ΔG° values for the three reactions shows that reaction 3 is so energetically favorable that it more than compensates for the other two energetically unfavorable reactions. Hence the overall reaction is indeed thermodynamically spontaneous as written.

| Note |
| --- |
| By coupling reactions, a reaction that is thermodynamically nonspontaneous can be made spontaneous. |

Example 15

Bronze Age metallurgists were accomplished practical chemists who unknowingly used coupled reactions to obtain metals from their ores. Realizing that different ores of the same metal required different treatments, they heated copper oxide ore in the presence of charcoal (carbon) to obtain copper metal, whereas they pumped air into the reaction system if the ore was copper sulfide. Assume that a particular copper ore consists of pure cuprous oxide ($Cu_2O$). Using the $\Delta G^\circ_f$ values given for each, calculate

a. $\Delta G°$ and $K_p$ for the decomposition of $Cu_2O$ to metallic copper and oxygen gas [$\Delta G^\circ_f(Cu_2O) = -146.0$ kJ/mol].

b. $\Delta G°$ and $K_p$ for the reaction of $Cu_2O$ with carbon to produce metallic copper and carbon monoxide [$\Delta G^\circ_f(CO) = -137.2$ kJ/mol].

**Given**: reactants and products, $\Delta G^\circ_f$ values for $Cu_2O$ and CO, and temperature

**Asked for**: $\Delta G°$ and $K_p$ for the formation of metallic copper from $Cu_2O$ in the absence and presence of carbon

**Strategy**:

A. Write the balanced equilibrium equation for each reaction. Using the "products minus reactants" rule, calculate $\Delta G°$ for the reaction.

B. Substitute appropriate values into Equation 18.36 to obtain $K_p$.

**Solution**

A The chemical equation for the decomposition of cuprous oxide is as follows:

$$Cu_2O(s) \rightleftharpoons 2Cu(s) + \tfrac{1}{2}O_2(g)$$

The substances on the right side of this equation are pure elements in their standard states, so their $\Delta G^\circ_f$ values are zero. $\Delta G°$ for the reaction is therefore

$$\Delta G^\circ = \left[2\Delta G^\circ_f(Cu) + \frac{1}{2}\Delta G^\circ_f(O_2)\right] - \Delta G^\circ_f(Cu_2O) \tag{18.7.3}$$

$$= \left[(2\text{ mol})(0\text{ kJ/mol}) + \left(\frac{1}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] - [(1\text{ mol})(-146.0\text{ kJ/mol})] \tag{18.7.4}$$

$$= 146.0\text{ kJ} \tag{18.7.5}$$

B Rearranging and substituting the appropriate values into Equation 18.36,

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{(146.0\text{ kJ})(1000\text{ J/kJ})}{(8.314\text{ J/K})(298.15\text{ K})} = -58.90 \tag{18.7.6}$$

$$K_p = 2.6 \times 10^{-26} \tag{18.7.7}$$

This is a very small number, indicating that $Cu_2O$ does not spontaneously decompose to a significant extent at room temperature.

b.

A The $O_2$ produced in the decomposition of $Cu_2O$ can react with carbon to form CO:

$$\tfrac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g)$$

Because $\Delta G°$ for this reaction is equal to $\Delta G^\circ_f$ for CO (−137.2 kJ/mol), it is energetically more feasible to produce metallic copper from cuprous oxide by coupling the two reactions:

$$Cu_2O(s) \rightleftharpoons 2Cu(s) + \frac{1}{2}O_2(g) \qquad \Delta G^\circ = 146.0\text{ kJ/mol} \tag{18.7.8}$$

$$\frac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g) \qquad \Delta G^\circ = -137.2\text{ kJ/mol} \tag{18.7.9}$$

$$Cu_2O(s) + C(s) \rightleftharpoons 2Cu(s) + CO(g) \qquad \Delta G^\circ_f = 8.8\text{ kJ/mol} \tag{18.7.10}$$

B We can find the corresponding value of $K_p$:

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{(8.8\text{ kJ})(1000\text{ J/kJ})}{(8.314\text{ J/K})(298.15\text{ K})} = -3.6 \tag{18.7.11}$$

$$K_p = 0.03 \tag{18.7.12}$$

Although this value is still less than 1, indicating that reactants are favored over products at room temperature, it is about 24 orders of magnitude greater than $K_p$ for the production of copper metal in the absence of carbon. Because both $\Delta H°$ and $\Delta S°$ are positive for this reaction, it becomes thermodynamically feasible at slightly elevated temperatures (greater than about 80°C). At temperatures of a few hundred degrees Celsius, the reaction occurs spontaneously, proceeding smoothly and rapidly to the right as written and producing metallic copper and carbon monoxide from cuprous oxide and carbon.

Exercise 1

Use the $\Delta G^\circ_f$ values given to calculate $\Delta G°$ and $K_p$ for each reaction.

a. the decomposition of cuprous sulfide to copper metal and elemental sulfur [$\Delta G^\circ_f(Cu_2S) = -86.2$ kJ/mol]

b. the reaction of cuprous sulfide with oxygen gas to produce sulfur dioxide and copper metal [$\Delta G^\circ_f[SO_2(g)] = -300.1$ kJ/mol]

Answer:

a. $\Delta G° = 86.2$ kJ/mol; $K_p = 7.90 \times 10^{-16}$

b. $\Delta G° = -213.9$ kJ/mol; $K_p = 2.99 \times 10^{37}$

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# 18.8: Thermodynamics and Life

**Learning Objectives**

- To understand the importance of thermodynamics in biochemical systems.

In a thermodynamic sense, a living cell can be viewed as a low-entropy system that is *not* in equilibrium with its surroundings and is capable of replicating itself. A constant input of energy is needed to maintain the cell's highly organized structure, its wide array of precisely folded biomolecules, and its intricate system of thousands of chemical reactions. A cell also needs energy to synthesize complex molecules from simple precursors (e.g., to make proteins from amino acids), create and maintain differences in the concentrations of various substances inside and outside the cell, and do mechanical work (e.g., muscle contraction). In this section, we examine the nature of the energy flow between a cell and its environment as well as some of the chemical strategies cells use to extract energy from their surroundings and store that energy.

## Energy Flow between a Cell and Its Surroundings

One implication of the first and second laws of thermodynamics is that any closed system must eventually reach equilibrium. With no external input, a clock will run down, a battery will lose its charge, and a mixture of an aqueous acid and an aqueous base will achieve a uniform intermediate pH value. In contrast, a cell is an open system that can exchange matter with its surroundings as well as absorb energy from its environment in the form of heat or light. Cells use the energy obtained in these ways to maintain the nonequilibrium state that is essential for life.

Because cells are open systems, they cannot be described using the concepts of classical thermodynamics that we have discussed in this chapter, which have focused on reversible processes occurring in closed chemical systems that can exchange energy—but not matter—with their surroundings. Consequently, a relatively new subdiscipline called *nonequilibrium thermodynamics* has been developed to quantitatively describe open systems such as living cells.

Because a cell cannot violate the second law of thermodynamics, the only way it can maintain a low-entropy, nonequilibrium state characterized by a high degree of structural organization is to increase the entropy of its surroundings. A cell releases some of the energy that it obtains from its environment as heat that is transferred to its surroundings, thereby resulting in an increase in $S_{surr}$ (Figure 18.8.1). As long as $\Delta S_{surr}$ is positive and greater than $\Delta S_{sys}$, the entropy of the universe increases, so the second law of thermodynamics is not violated. Releasing heat to the surroundings is necessary but not sufficient for life: the release of energy must be coupled to processes that increase the degree of order within a cell. For example, a wood fire releases heat to its surroundings, but unless energy from the burning wood is also used to do work, there is no increase in order of any portion of the universe.

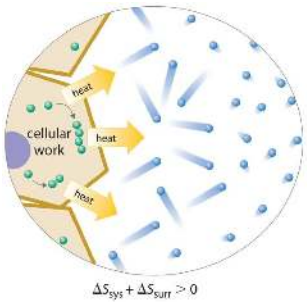



Figure 18.8.1 Life and **Entropy** A living cell is in a low-entropy, nonequilibrium state characterized by a high degree of structural organization. To maintain this state, a cell must release some of the energy it obtains from its environment as heat, thereby increasing $S_{surr}$ sufficiently that the second law of thermodynamics is not violated. In this example, the cell combines smaller components into larger, more ordered structures; the accompanying release of heat increases the entropy of the surrounding environment so that $S_{univ} > 0$.

### Note the Pattern

Any organism in equilibrium with its environment is dead.

## Extracting Energy from the Environment

Although organisms employ a wide range of specific strategies to obtain the energy they need to live and reproduce, they can generally be divided into two categories: organisms are either *phototrophs* (from the Greek *photos*, meaning "light," and *trophos*, meaning "feeder"), whose energy source is sunlight, or *chemotrophs*, whose energy source is chemical compounds, usually obtained by consuming or breaking down other organisms. Phototrophs, such as plants, algae, and photosynthetic bacteria, use the radiant energy of the sun directly, converting water and carbon dioxide to energy-rich organic compounds, whereas chemotrophs, such as animals, fungi, and many nonphotosynthetic bacteria, obtain energy-rich organic compounds from their environment. Regardless of the nature of their energy and carbon sources, all organisms use oxidation–reduction, or redox, reactions to drive the synthesis of complex biomolecules. Organisms that can use only $O_2$ as the oxidant (a group that includes most animals) are *aerobic organisms* that cannot survive in the absence of $O_2$. Many organisms that use other oxidants (such as $SO_4^{2-}$, $NO_3^-$, or $CO_3^{2-}$) or oxidized organic compounds can live only in the absence of $O_2$, which is a deadly poison for them; such species are called *anaerobic organisms*.

The fundamental reaction by which all green plants and algae obtain energy from sunlight is photosynthesisThe fundamental reaction by which all green plants and algae obtain energy from sunlight in which $CO_2$ is photochemically reduced to a carbon compound such as glucose. Oxygen in water is concurrently oxidized to $O_2$, the photochemical reduction of $CO_2$ to a carbon compound such as glucose. Concurrently, oxygen in water is oxidized to $O_2$ (recall that *h*ν is energy from light):

$$6CO_2 + 6H_2O \xrightarrow[photosynthesis]{h\nu} C_6H_{12}O_6 + 6O_2$$

This reaction is not a spontaneous process as written, so energy from sunlight is used to drive the reaction. Photosynthesis is critical to life on Earth; it produces all the oxygen in our atmosphere.

In many ways, chemotrophs are more diverse than phototrophs because the nature of both the reductant (the nutrient) and the oxidant can vary. The most familiar chemotrophic strategy uses compounds such as glucose as the reductant and molecular oxygen as the oxidant in a process called respirationA process by which chemotrophs obtain energy from their environment; the overall reaction of respiration is the reverse of photosynthesis. Respiration is the combustion of a carbon compound such as glucose to $CO_2$ and water. The overall reaction of respiration is the reverse of photosynthesis:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

An alternative strategy uses fermentationA process used by some chemotrophs to obtain energy from their environment; a chemical reaction in which both the oxidant and the reductant are organic compounds. reactions, in which an organic compound is simultaneously oxidized and reduced. Common examples are alcohol fermentation, used in making wine, beer, and bread, and lactic acid fermentation, used in making yogurt:

$$C_6H_{12}O_6 \underset{alcohol\,fermentation}{\rightarrow} 2CO_2 + 2CH_3CH_2OH$$

$$C_6H_{12}O_6 \underset{lactic\,acid\,fermentation}{\rightarrow} 2CH_3CH\left(OH\right)CO_2H$$

In these reactions, some of the carbon atoms of glucose are oxidized, while others are reduced. Recall that a reaction in which a single species is both oxidized and reduced is called a *disproportionation* reaction.

## The Role of NADH and ATP in Metabolism

Regardless of the identity of the substances from which an organism obtains energy, the energy must be released in very small increments if it is to be useful to the cell. Otherwise, the temperature of the cell would rise to lethal levels. Cells store part of the energy that is released as ATP (adenosine triphosphate), a compound that is the universal energy currency of all living organisms (Figure 18.8.2).

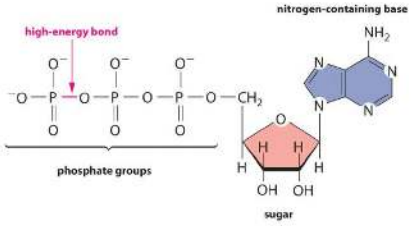



Figure 18.8.2 ATP, the Universal Energy Currency of All **Cells** The ATP molecule contains a nitrogen-containing base, a sugar, and three phosphate groups, as well as two high-energy phosphoric acid anhydride bonds.

Most organisms use several intermediate species to shuttle electrons between the terminal reductant (such as glucose) and the terminal oxidant (such as $O_2$). In virtually all cases, an intermediate species oxidizes the energy-rich reduced compound, and the now-reduced intermediate then migrates to another site where *it* is oxidized. The most important of these electron-carrying intermediates is $NAD^+$ (nicotinamide adenine dinucleotide; Figure 18.19), whose reduced form, formally containing $H^-$, is NADH (reduced nicotinamide adenine dinucleotide). The reduction of $NAD^+$ to NADH can be written as follows:

$$NAD^+ + H^+ \rightarrow NADH$$

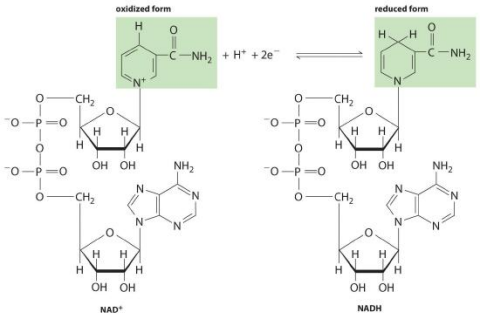



Figure 18.8.3 $NAD^+$ and Its Reduced Form (NADH)This electron carrier is used by biological systems to transfer electrons from one species to another. The oxidized form ($NAD^+$) is reduced to NADH by energy-rich nutrients such as glucose, and the reduced form (NADH), is then oxidized to $NAD^+$ by $O_2$ during respiration.

Most organisms use $NAD^+$ to oxidize energy-rich nutrients such as glucose to $CO_2$ and water; NADH is then oxidized to $NAD^+$ using an oxidant such as $O_2$. During oxidation, a fraction of the energy obtained from the oxidation of the nutrient is stored as ATP. The phosphoric acid anhydride bonds in ATP can then be hydrolyzed by water, releasing energy and forming ADP (adenosine diphosphate). It is through this sequence of reactions that energy from the oxidation of nutrients is made available to cells. Thus ATP has a central role in metabolism: it is synthesized by the oxidation of nutrients, and its energy is then used by cells to drive synthetic reactions and perform work (Figure 18.8.4).

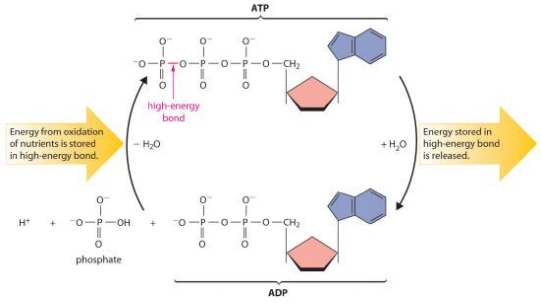



Figure 18.8.5 The ATP Cycle The high-energy phosphoric acid anhydride bond in ATP stores energy released during the oxidation of nutrients. Hydrolysis of the high-energy bond in ATP releases energy, forming adenosine diphosphate (ADP) and phosphate.

Under standard conditions in biochemical reactions, all reactants are present in aqueous concentrations of 1 M at a pressure of 1 atm. For $H^+$, this corresponds to a pH of zero, but very little biochemistry occurs at pH = 0. For biochemical reactions, chemists have therefore defined a new standard state in which the $H^+$ concentration is $1 \times 10^{-7}$ M (pH 7.0), and all other reactants and products are present in their usual standard-state conditions (1 M or 1 atm). The free-energy change and corresponding equilibrium constant for a reaction under these new standard conditions are denoted by the addition of a prime sign (′) to the conventional

symbol: $\Delta G°'$ and $K'$. If protons do not participate in a biological reaction, then $\Delta G°' = \Delta G°$. Otherwise, the relationship between $\Delta G°'$ and $\Delta G°$ is as follows:

$$\Delta G^{o\prime} = \Delta G^{o} + RTln\left(10^{-7}\right)^{n}$$

where $\Delta G°'$ and $\Delta G°$ are in kilojoules per mole and $n$ is the number of protons produced in the reaction. At 298 K, this simplifies to

$$\Delta G^{o\prime} = \Delta G^{o} - 39.96n$$

Thus any reaction that involves the release of protons is thermodynamically more favorable at pH 7 than at pH 0.

The chemical equation that corresponds to the hydrolysis of ATP to ADP and phosphate is as follows:

$$ATP^{4-} + H_2O \rightleftharpoons ATP^{3-} + HPO_4^{2-} + H^+$$

This reaction has a $\Delta G°'$ of −34.54 kJ/mol, but under typical physiological (or biochemical) conditions, the actual value of $\Delta G'$ for the hydrolysis of ATP is about −50 kJ/mol. Organisms use this energy to drive reactions that are energetically uphill, thereby coupling the reactions to the hydrolysis of ATP. One example is found in the biochemical pathway of *glycolysis*, in which the 6-carbon sugar glucose ($C_6H_{12}O_6$) is split into two 3-carbon fragments that are then used as the fuel for the cell. Initially, a phosphate group is added to glucose to form a phosphate ester, glucose-6-phosphate (abbreviated glucose-6-P), in a reaction analogous to that of an alcohol and phosphoric acid:

$$glucose\,(aq) + HPO_4^{2-}\,(aq) \rightleftharpoons glucose - 6 - P^{2-}\,(aq) + H_2O\,(l)$$
$$ROH\,(aq) + HOPO_3^{2-}\,(aq) \rightleftharpoons ROPO_3^{2-}\,(aq) + H_2O\,(l)$$

Due to its electrical charge, the phosphate ester is unable to escape from the cell by diffusing back through the membrane surrounding the cell, ensuring that it remains available for further reactions. For the reaction in Equation 18.57, $\Delta G°$ is 17.8 kJ/mol and $K$ is $7.6 \times 10^{-4}$, indicating that the equilibrium lies far to the left. To force this reaction to occur as written, it is coupled to a thermodynamically favorable reaction, the hydrolysis of ATP to ADP:

$$glucose + \cancel{HPO_4^{2-}} \rightleftharpoons glucose - 6 - P^{2-} + \cancel{H_2O} \qquad \Delta G^{o\prime} = 17.8\ kJ/mol \qquad K_1$$

$$ATP^{4-} + \cancel{H_2O} \rightleftharpoons ATP^{3-} + \cancel{HPO_4^{2-}} + H^+ \qquad \Delta G^{o\prime} = -34.54\ kJ/mol \qquad K_2$$

$$glucose + ATP^{4-} \rightleftharpoons glucose - 6 - P^{2-} + ATP^{3-} + H^+ \qquad \Delta G^{o\prime} = -16.7\ kJ/mol \qquad K_3$$

Thus the formation of glucose-6-phosphate is thermodynamically spontaneous if ATP is used as the source of phosphate.

### Note the Pattern

Organisms use energy from the hydrolysis of ATP to drive reactions that are thermodynamically nonspontaneous.

The formation of glucose-6-phosphate is only one of many examples of how cells use ATP to drive an otherwise nonspontaneous biochemical reaction. Under nonstandard physiological conditions, each ATP hydrolyzed actually results in approximately a $10^8$ increase in the magnitude of the equilibrium constant, compared with the equilibrium constant of the reaction in the absence of ATP. Thus a reaction in which two ATP molecules are converted to ADP increases $K$ by about $10^{16}$, three ATP molecules by $10^{24}$, and so forth. Virtually any energetically unfavorable reaction or sequence of reactions can be made to occur spontaneously by coupling it to the hydrolysis of a sufficiently large number of ATP molecules.

## Energy Storage in Cells

Although all organisms use ATP as the *immediate* free-energy source in biochemical reactions, ATP is not an efficient form in which to store energy on a long-term basis. If the caloric intake of an average resting adult human were stored as ATP, two-thirds of the body weight would have to consist of ATP. Instead, a typical 70 kg adult human has a total of only about 50 g of both ATP and ADP, and, far from being used for long-term storage, each molecule of ATP is turned over about 860 times per day. The entire ATP supply would be exhausted in less than 2 minutes if it were not continuously regenerated.

How does the body store energy for the eventual production of ATP? Three primary means are as sugars, proteins, and fats. The combustion of sugars and proteins yields about 17 kJ of energy per gram, whereas the combustion of fats yields more than twice as much energy per gram, about 39 kJ/g. Moreover, sugars and proteins are hydrophilic and contain about 2 g of water per gram of

fuel, even in very concentrated form. In contrast, fats are hydrophobic and can be stored in essentially anhydrous form. As a result, organisms can store about six times more energy per gram as fats than in any other form. A typical 70 kg adult human has about 170 kJ of energy in the form of glucose circulating in the blood, about 2600 kJ of energy stored in the muscles and liver as glycogen (a polymeric form of glucose), about 100,000 kJ stored in the form of protein (primarily muscle tissue), and almost 500,000 kJ in the form of fats (Figure 18.21). Thus fats constitute by far the greatest energy reserve, while accounting for only about 12 kg of the 70 kg body mass. To store this amount of energy in the form of sugars would require a total body mass of about 144 kg, more than half of which would be sugar.

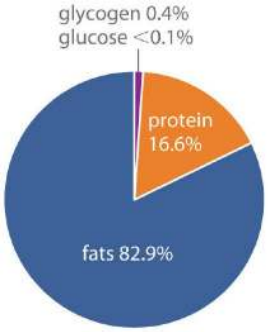



Figure 18.8.6 Percentages of Forms of Energy Storage in Adult Humans An average 70 kg adult stores about $6 \times 10^5$ kJ of energy in glucose, glycogen, protein, and fats. Fats are the most abundant and most efficient form for storing energy.

## Example 18.8.1

Glucose is one form in which the body stores energy.

1. Calculate $\Delta G°'$ for the respiration of glucose to $CO_2$ and $H_2O$ using these values of $\Delta G_f°$: −910.4 kJ/mol for glucose, −394.4 kJ/mol for $CO_2$(g), and −237.1 kJ/mol for $H_2O$(l).
2. Assuming 50% efficiency in the conversion of the released energy to ATP, how many molecules of ATP can be synthesized by the combustion of one molecule of glucose? At 298.15 K, $\Delta G°'$ for the hydrolysis of ATP is −34.54 kJ/mol.

**Given:** balanced chemical equation (Equation 18.50), values of $\Delta G_f°$, conversion efficiency, and $\Delta G°'$ for hydrolysis of ATP

**Asked for:** $\Delta G°'$ for the combustion reaction and the number of molecules of ATP that can be synthesized

**Strategy:**

**A** Using the "products minus reactants" rule, calculate $\Delta G_{rxn}°$ for the respiration reaction.

**B** Multiply the calculated value of $\Delta G_{rxn}°$ by the efficiency to obtain the number of kilojoules available for ATP synthesis. Then divide this value by $\Delta G°'$ for the hydrolysis of ATP to find the maximum number of ATP molecules that can be synthesized.

**Solution:**

1. **A** Protons are not released or consumed in the reaction, so $\Delta G°' = \Delta G°$. We begin by using the balanced chemical equation in Equation 18.50: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

   From the given values of $\Delta G_f°$ (remember that $\Delta G_f°$ is zero for an element such as $O_2$ in its standard state), we can calculate $\Delta G_{rxn}°$

   $$\Delta G^o_{rxn} = \sum m\Delta G^o_f\,(products) - \sum n\Delta G^o_f\,(reactants-)$$

   $$= [6\,(-394.4\ kJ/mol) + 6\,(-237.1\ kJ/mol)] - [(910.4\ kJ/mol) + 0\ kJ/mol]$$

   $$= -2879\ kJ/mol\ of\ glucose$$

2. **B** If we assume that only 50% of the available energy is used, then about 1440 kJ/mol of glucose is available for ATP synthesis. The value of $\Delta G°'$ for the hydrolysis of ATP under biochemical conditions is −34.54 kJ/mol, so in principle an organism could synthesize $\dfrac{1440\ \cancel{kJ/mol\ glucose}}{34.54\ \cancel{kJ/mol\ ATP}} = 41.7 \approx 42\ ATP/glucose$

   Most aerobic organisms actually synthesize about 32 molecules of ATP per molecule of glucose, for an efficiency of about 45%.

Exercise

Some bacteria synthesize methane using the following redox reaction:

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g)$$

1. Calculate $\Delta G°$ for this reaction using values of $\Delta G_f°$ in Table T1.
2. Calculate how many ATP molecules could be synthesized per mol of $CO_2$ reduced if the efficiency of the process were 100%.

**Answer**

1. −86.6 kJ/mol $CO_2$
2. 2.5 ATP/mol $CO_2$

## Summary

A living cell is a system that is not in equilibrium with its surroundings; it requires a constant input of energy to maintain its nonequilibrium state. Cells maintain a low-entropy state by increasing the entropy of their surroundings. *Aerobic organisms* cannot survive in the absence of $O_2$, whereas *anaerobic organisms* can live only in the absence of $O_2$. Green plants and algae are *phototrophs*, which extract energy from the environment through a process called **photosynthesis**, the photochemical reduction of $CO_2$ to a reduced carbon compound. Other species, called *chemotrophs*, extract energy from chemical compounds. One of the main processes chemotrophs use to obtain energy is **respiration**, which is the reverse of photosynthesis. Alternatively, some chemotrophs obtain energy by **fermentation**, in which an organic compound is both the oxidant and the reductant. Intermediates used by organisms to shuttle electrons between the reductant and the oxidant include $NAD^+$ and NADH. Energy from the oxidation of nutrients is made available to cells through the synthesis of ATP, the energy currency of the cell. Its energy is used by cells to synthesize substances through coupled reactions and to perform work. The body stores energy as sugars, protein, or fats before using it to produce ATP.

## Conceptual Problem

1. The tricarboxylic acid (TCA) cycle in aerobic organisms is one of four pathways responsible for the stepwise oxidation of organic intermediates. The final reaction in the TCA cycle has $\Delta G° = 29.7$ kJ/mol, so it should not occur spontaneously. Suggest an explanation for why this reaction proceeds in the forward direction in living cells.

## Answer

1. It is coupled to another reaction that is spontaneous, which drives this reaction forward (Le Chatelier's principle).

## Contributors

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# CHAPTER OVERVIEW

## 19: Electrochemistry




**Howard University**

**General Chemistry:**
**An Atoms First Approach**



19.1: Introduction
19.2: Describing Electrochemical Cells
19.3: Standard Potentials
19.4: Comparing Strengths of Oxidants and Reductants
19.5: Electrochemical Cells and Thermodynamics
19.6: Commercial Galvanic Cells
19.7: Corrosion
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# 19.1: Introduction

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In oxidation–reduction (redox) reactions, electrons are transferred from one species (the reductant) to another (the oxidant). This transfer of electrons provides a means for converting chemical energy to electrical energy or vice versa. The study of the relationship between electricity and chemical reactions is called electrochemistry (the study of the relationship between electricity and chemical reactions., an area of chemistry we introduced in Chapter 8 and Chapter 9). In this chapter, we describe electrochemical reactions in more depth and explore some of their applications.

In the first three sections, we review redox reactions; describe how they can be used to generate an electrical potential, or *voltage*; and discuss factors that affect the magnitude of the potential. We then explore the relationships among the electrical potential, the change in free energy, and the equilibrium constant for a redox reaction, which are all measures of the thermodynamic driving force for a reaction. Finally, we examine two kinds of applications of electrochemical principles: (1) those in which a spontaneous reaction is used to provide electricity and (2) those in which electrical energy is used to drive a thermodynamically nonspontaneous reaction. By the end of this chapter, you will understand why different kinds of batteries are used in cars, flashlights, cameras, and portable computers; how rechargeable batteries operate; and why corrosion occurs and how to slow—if not prevent—it. You will also discover how metal objects can be plated with silver or chromium for protection; how silver polish removes tarnish; and how to calculate the amount of electricity needed to produce aluminum, chlorine, copper, and sodium on an industrial scale.



**A view from the top of the Statue of Liberty, showing the green patina coating the statue.** The patina is formed by corrosion of the copper skin of the statue, which forms a thin layer of an insoluble compound that contains copper(II), sulfate, and hydroxide ions.

## Contributors

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# 19.2: Describing Electrochemical Cells

**Learning Objectives**

- To distinguish between galvanic and electrolytic cells.

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. As we described in Chapter 7, a redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The reductant (a substance that is capable of donating electrons and in the process is oxidized) is the substance that loses electrons and is oxidized in the process; the oxidant (A substance that is capable of accepting electrons and in the process is reduced) is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions (reactions that represent either the oxidation half or the reduction half of an oxidation–reduction (redox) reaction), one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$Zn\,(s) + Br_2\,(l) \rightarrow Zn^{2+}\,(aq) + 2Br^-\,(aq) \tag{19.1.1}$$

The half-reactions are as follows:

$$reduction\ half\ reaction: Br_2\,(l) + 2e^- \rightarrow 2Br^-\,(aq) \tag{19.1.2}$$

$$oxidation\ half\ reaction: Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^- \tag{19.1.3}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the reductant in this reaction (it loses electrons), and $Br_2$ is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 19.1). A redox reaction is balanced when *the number of electrons lost by the reductant equals the number of electrons gained by the oxidant*. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

### Note the Pattern

In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an electrochemical cell (an apparatus that generates electricity from a spontaneous oxidation–reduction (redox) reaction or, conversely, uses electricity to drive a nonspontaneous redox reaction).

There are two types of electrochemical cells: galvanic cells and electrolytic cells. A galvanic (voltaic) cell (an electrochemical cell that uses the energy released during a spontaneous oxidation–reduction (redox) reaction ($\Delta G^o$) to generate electricity). Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to *generate* electricity. This type of electrochemical cell is often called a *voltaic cell* after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an electrolytic cellAn electrochemical cell that consumes electrical energy from an external source to drive a nonspontaneous ($\Delta G^o$) oxidation–reduction (redox) reaction. *consumes* electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two electrodesA solid metal connected by an electrolyte and an external circuit that provides an electrical connection between systems in an electrochemical cell (galvanic or electrolytic)., which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 19.1.1). The oxidation half-reaction occurs at one electrode (the anodeOne of two electrodes in an electrochemical cell, it is the site of the oxidation half-reaction.), and the reduction half-reaction occurs at the other (the cathodeOne of two electrodes in an electrochemical cell, it is the site of the reduction half-reaction.). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an *electrolyte*, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells. We discuss electrolytic cells in Section 19.7.

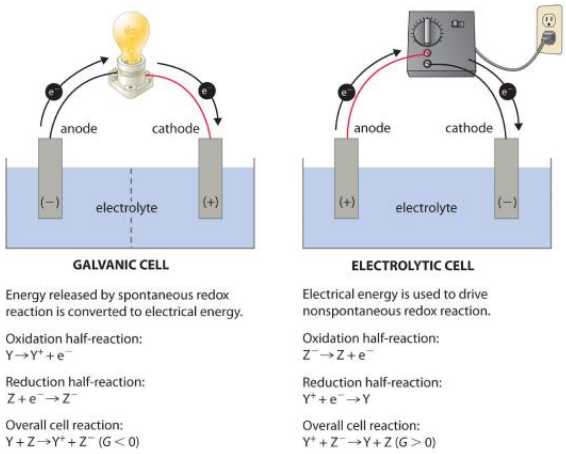



Figure 19.1.1 Electrochemical **Cells** A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

## Galvanic (Voltaic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion ($Cu^{2+}$) to give copper metal and $Zn^{2+}$ ion. The balanced chemical equation is as follows:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

We can cause this reaction to occur by inserting zinc powder into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc dissolves, and a mass of metallic copper forms (Figure 19.1.2). These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



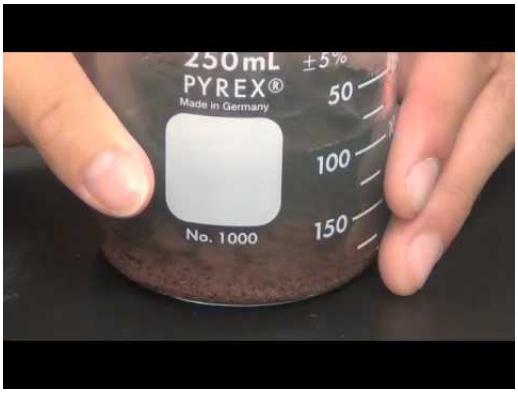



**Figure 19.1.2 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment** When zinc powder is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $Zn^{2+}$(aq) ions, while $Cu^{2+}$(aq) ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. The reaction demonstration starts at 3:00 in the video, the chemistry of the reaction is discussed in the first three minutes and at the end

This same reaction can be carried out using the galvanic cell illustrated in part (a) in Figure 19.1.3. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $Cu^{2+}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $Zn^{2+}$ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a salt bridge (a U-shaped tube inserted into both solutions of a galvanic cell that contains a concentrated liquid or gelled electrolyte and completes the circuit between the anode and the cathode), a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are $Na^+$ or $K^+$ and $NO_3^-$ or $SO_4^{2-}$, respectively. (The ions in the salt bridge do *not* have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to $Zn^{2+}$ ions at the zinc electrode (the anode), and $Cu^{2+}$ ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of $Zn^{2+}$ ions in the $Zn^{2+}$ solution increases; simultaneously, the copper strip gains mass, and the concentration of $Cu^{2+}$ ions in the $Cu^{2+}$ solution decreases (part (b) in Figure 19.1.3). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

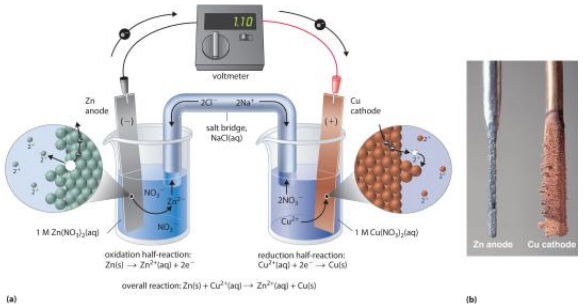



Figure 19.1.3 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of $Cu^{2+}$ ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of $Zn^{2+}$ ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to $Zn^{2+}$ ions in the left compartment, while $Cu^{2+}$ ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give $Zn^{2+}$(aq) ions, while the Cu cathode gains mass as $Cu^{2+}$(aq) ions are reduced to copper metal that is deposited on the cathode.

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the $Zn^{2+}$ solution would increase as the zinc metal dissolves, and the total positive charge in the $Cu^{2+}$ solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the $Zn^{2+}$ solution and a flow of cations into the $Cu^{2+}$ solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

**A galvanic cell.** This galvanic ıse of a salt bridge to connect two solutions generating a voltage.

A *voltmeter* can be used to m  e in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode p om flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current anode to the cathode. The potential ($E_{cell}$)Related to the energy needed to move a charged particle in an electric field, it is the diff potential beween two half-reactions. of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (part (a) in Figure 19.1.3 ). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 1.

### Note the Pattern

A galvanic (voltaic) cell converts the energy released by a spontaneous chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a nonspontaneous chemical reaction.

### Example 19.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

For this galvanic cell,

1. write the half-reaction that occurs at each electrode.
2. indicate which electrode is the cathode and which is the anode.
3. indicate which electrode is the positive electrode and which is the negative electrode.

**Given:** galvanic cell and redox reaction

**Asked for:** half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

**Strategy:**

**A** Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.

**B** From the direction of electron flow, assign each electrode as either positive or negative.

**Solution:**

1. **A** In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form $NO_2$, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows: reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

   Thus nitrate is reduced to NO, while the tin electrode is oxidized to $Sn^{2+}$.
2. Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.
3. **B** Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow *from* the tin electrode, it must be electrically negative. In contrast, electrons flow *toward* the Pt electrode, so that electrode must be electrically positive.

Exercise

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $MnO_4^-$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $Sn^{2+}$ in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2MnO_4^-(aq) + 5Sn^{2+}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$

For this galvanic cell,

1. write the half-reaction that occurs at each electrode.
2. indicate which electrode is the cathode and which is the anode.
3. indicate which electrode is positive and which is negative.

**Answer**

1. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$
2. The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.
3. The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

## Constructing a Cell Diagram

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a *cell diagram*, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in part (a) in Figure 19.1.3 is written as follows:

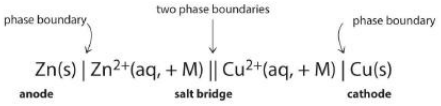



**Figure 19.1.4** A cell diagram includes solution concentrations when they are provided.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the *junction potential*. One example of this type of galvanic cell is as follows:

$$Pt\,(s) \mid H_2\,(g) \mid HCl\,(aq) \mid AgCl\,(s) \mid Ag\,(s)$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

$$cathode\ reaction: AgCl\,(s) + e^- \rightarrow Ag\,(s) + Cl^-\,(aq)$$

$$anode\ reaction: \frac{1}{2}H_2\,(g) \rightarrow H^+\,(aq) + e^-$$

$$overall: AgCl\,(s) + \frac{1}{2}H_2\,(g) \rightarrow Ag\,(s) + Cl^-\,(aq) + H^+\,(aq)$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

### Example 19.1.2

Draw a cell diagram for the galvanic cell described in Example 1. The balanced chemical reaction is as follows:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

**Given:** galvanic cell and redox reaction

**Asked for:** cell diagram

**Strategy:**

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

**Solution:**

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $Sn(s)\,|\,Sn^{2+}(aq)$. We could include $H_2SO_4(aq)$ with the contents of the anode compartment, but the sulfate ion (as $HSO_4^-$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$Sn(s)\,|\,Sn^{2+}(aq)\,\|\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise

Draw a cell diagram for the following reaction, assuming the concentration of $Ag^+$ and $Mg^{2+}$ are each 1 M:

$$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$$

**Answer:** $Mg(s)|Mg^{2+}(aq, 1\ M)\|Ag^+(aq, 1\ M)|Ag(s)$

## Summary

**Electrochemistry** is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two **half-reactions**, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the **reductant** equals the number of electrons gained by the **oxidant**. An electric current is produced from the flow of electrons from the reductant to the oxidant. An **electrochemical cell** can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a **galvanic (voltaic) cell**, the energy from a spontaneous reaction generates electricity, whereas in an **electrolytic cell**, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two **electrodes** that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the **anode**, and the reductive half-reaction occurs at the **cathode**. A **salt bridge** connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The **potential** of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

## Key Takeaway

- A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur.

## Conceptual Problems

1. Is $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ an oxidation–reduction reaction? Why or why not?
2. If two half-reactions are physically separated, how is it possible for a redox reaction to occur? What is the name of the apparatus in which two half-reactions are carried out simultaneously?
3. What is the difference between a galvanic cell and an electrolytic cell? Which would you use to generate electricity?
4. What is the purpose of a salt bridge in a galvanic cell? Is it always necessary to use a salt bridge in a galvanic cell?
5. One criterion for a good salt bridge is that it contains ions that have similar rates of diffusion in aqueous solution, as $K^+$ and $Cl^-$ ions do. What would happen if the diffusion rates of the anions and cations differed significantly?
6. It is often more accurate to measure the potential of a redox reaction by immersing two electrodes in a single beaker rather than in two beakers. Why?

## Answer

1.
2.
3.
4.
5. A large difference in cation/anion diffusion rates would increase resistance in the salt bridge and limit electron flow through the circuit.
6.

## Numerical Problems

1. Copper(I) sulfate forms a bright blue solution in water. If a piece of zinc metal is placed in a beaker of aqueous $CuSO_4$ solution, the blue color fades with time, the zinc strip begins to erode, and a black solid forms around the zinc strip. What is happening? Write half-reactions to show the chemical changes that are occurring. What will happen if a piece of copper metal is placed in a colorless aqueous solution of $ZnCl_2$?
2. Consider the following spontaneous redox reaction: $NO_3^-(aq) + H^+(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + HNO_2(aq)$.
    1. Write the two half-reactions for this overall reaction.
    2. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which electrode corresponds to which half-reaction?
    3. Which electrode is negatively charged, and which is positively charged?
3. The reaction $Pb(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow Pb^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$ occurs spontaneously.
    1. Write the two half-reactions for this redox reaction.

2. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which reaction occurs at the cathode and which occurs at the anode?
3. Which electrode is positively charged, and which is negatively charged?

4. Phenolphthalein is an indicator that turns pink under basic conditions. When an iron nail is placed in a gel that contains $[Fe(CN)_6]^{3-}$, the gel around the nail begins to turn pink. What is occurring? Write the half-reactions and then write the overall redox reaction.
5. Sulfate is reduced to $HS^-$ in the presence of glucose, which is oxidized to bicarbonate. Write the two half-reactions corresponding to this process. What is the equation for the overall reaction?
6. Write the spontaneous half-reactions and the overall reaction for each proposed cell diagram. State which half-reaction occurs at the anode and which occurs at the cathode.
   1. $Pb(s)\,|\,PbSO_4(s)\,|\,SO_4^{2-}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$
   2. $Hg(l)\,|\,Hg_2Cl_2(s)\,|\,Cl^-(aq)\,\|\,Cd^{2+}(aq)\,|\,Cd(s)$
7. For each galvanic cell represented by these cell diagrams, determine the spontaneous half-reactions and the overall reaction. Indicate which reaction occurs at the anode and which occurs at the cathode.
   1. $Zn(s)\,|\,Zn^{2+}(aq)\,\|\,H^+(aq)\,|\,H_2(g)$, Pt(s)
   2. $Ag(s)\,|\,AgCl(s)\,|\,Cl^-(aq)\,\|\,H^+(aq)\,|\,H_2(g)\,|\,Pt(s)$
   3. $Pt(s)\,|\,H_2(g)\,|\,H^+(aq)\,\|\,Fe^{2+}(aq)$, $Fe^{3+}(aq)\,|\,Pt(s)$
8. For each redox reaction, write the half-reactions and draw the cell diagram for a galvanic cell in which the overall reaction occurs spontaneously. Identify each electrode as either positive or negative.
   1. $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$
   2. $Fe^{3+}(aq) + 1/2H_2(g) \rightarrow Fe^{2+}(aq) + H^+(aq)$
9. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.
   1. $2Cl^-(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^-(aq)$
   2. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$
   3. $2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$
   4. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
10. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.
    1. $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$
    2. $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq) \rightarrow 2H_2O(l) + 4Fe^{3+}(aq)$
    3. $6Hg^{2+}(aq) + 2NO_3^-(aq) + 8H^+ \rightarrow 3Hg_2^{2+}(aq) + 2NO(g) + 4H_2O(l)$
    4. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

## Answers

1.
2.
3.
4.
5. reduction: $SO_4^{2-}(aq) + 9H^+(aq) + 8e^- \rightarrow HS^-(aq) + 4H_2O(l)$ oxidation: $C_6H_{12}O_6(aq) + 12H_2O(l) \rightarrow 6HCO_3^-(g) + 30H^+(aq) + 24e^-$ overall: $C_6H_{12}O_6(aq) + 3SO_4^{2-}(aq) \rightarrow 6HCO_3^-(g) + 3H^+(aq) + 3HS^-(aq)$
6.
7. 1. reduction: $2H^+(aq) + 2e^- \rightarrow H_2(aq)$; cathode;

      oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; anode;

      overall: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(aq)$
   2. reduction: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$; cathode;

      oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

      overall: $AgCl(s) + H_2(g) \rightarrow 2H^+(aq) + Ag(s) + Cl^-(aq)$
   3. reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$; cathode;

      oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

overall: $2Fe^{3+}(aq) + H_2(g) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$

8.
9.
10.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

Figure 9.1.2 the reaction between Zn and $Cu^{2+}$ from YouTube courtesy of UC Berkeley Chemistry and Respect Chemistry

Galvanic Cell demonstration from YouTube courtesy of Angela Stott

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# 19.3: Standard Potentials

**Learning Objectives**

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the *s* electrons of zinc by the electrons in filled *d* orbitals. (For more information on atomic orbitals, see Section 2.5.) Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper (Figure 19.2.1). Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

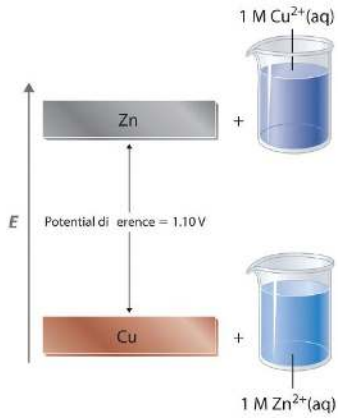



Figure 19.2.1 Potential Energy Difference in the Zn/Cu System The potential energy of a system consisting of metallic Zn and aqueous $Cu^{2+}$ ions is greater than the potential energy of a system consisting of metallic Cu and aqueous $Zn^{2+}$ ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + $Cu^{2+}$(aq) system is higher in energy by 1.10 V than the Cu(s) + $Zn^{2+}$(aq) system, energy is released when electrons are transferred from Zn to $Cu^{2+}$ to form Cu and $Zn^{2+}$.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 19.1.3 but instead of copper use a strip of cobalt metal and 1 M $Co^{2+}$ in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the *concentrations* of the reacting species and the *temperature* of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the standard cell potentialThe potential of an electrochemical cell measured under standard conditions (1 M for solutions, 1 atm for gases, and pure solids or pure liquids for other substances) and at a fixed temperature (usually 298 K). ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions,Concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an *activity* of 1 rather than a concentration of 1 M. Corrections for nonideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

### Note the Pattern

Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.

## Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the *difference* between the potentials of two electrodes can be measured. (This is analogous to measuring absolute enthalpies or free energies. Recall from Chapter 18 that only *differences* in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential ($E°$) for the Zn/Cu system is 1.10 V, whereas $E°$ for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co\,(s)\mid Co^{2+}\,(aq,\ 1M)\parallel Cu^{2+}\,(aq,\ 1M)\mid Cu\,(s)$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of $Cu^{2+}$ in solution at the copper cathode.

All tabulated values of *standard electrode potentials* by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances. (Standard electrode potentials for various reduction reactions are given in Table P1.) The standard cell potential ($E°_{cell}$) is therefore the *difference* between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the *sum* of the two half-reactions. According to Equation 19.2.1, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

### Note the Pattern

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials: $E°_{cell} = E°_{cathode} - E°_{anode}$.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The standard hydrogen electrode (SHE)The electrode chosen as the reference for all other electrodes, which has been assigned a standard potential of 0 V and consists of a Pt wire in contact with an aqueous solution that contains 1 M $H^+$ in equilibrium with $H_2$ gas at a pressure of 1 atm at the Pt-solution interface. is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M $H^+$. The $[H^+]$ in solution is in equilibrium with $H_2$ gas at a pressure of 1 atm at the Pt-solution interface (Figure 19.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+\,(aq) + 2e^- \rightleftharpoons H_2\,(g)$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

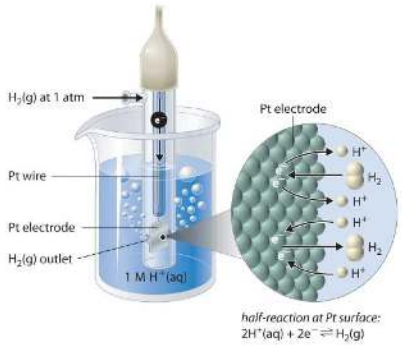



Figure 19.2.2 The Standard Hydrogen Electrode The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M $H^+$ in equilibrium with $H_2$ gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Figure 19.2.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of $Zn^{2+}$ ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form $Zn^{2+}$, and $H^+$ ions are reduced to $H_2$ in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn\,(s)\mid Zn^{2+}\,(aq)\parallel H^+\,(aq,\ 1M)\mid H_2\,(g, 1\ atm)\mid Pt\,(s)$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

$$cathode: 2H^+\,(aq,\ 1M) + 2e^- \rightarrow H_2\,(g) \quad E^o_{cathode} = 0\ V$$

$$anode: Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^- \quad E^o_{anode} = -0.76\ V$$

$$overall: Zn\,(s) + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.76$$

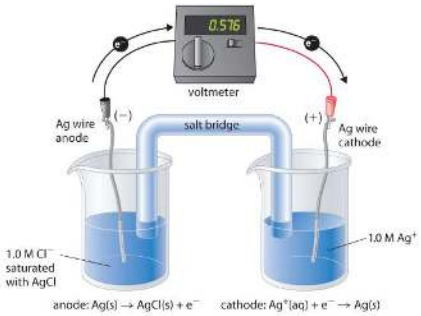



Figure 19.2.3 Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a $Zn/Zn^{2+}$ couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}$(aq) ions while $H^+$(aq) ions are reduced to $H_2$ at the platinum surface, the standard electrode potential of the $Zn^{2+}/Zn$ couple is −0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated $E°$ value is reported as a *reduction* potential. The potential of a half-reaction measured against the SHE under standard conditions is called the standard electrode potentialThe potential of a half-reaction measured against the SHE under standard conditions. for that half-reaction.In this example, the standard reduction potential for $Zn^{2+}$(aq) + 2e$^-$ → Zn(s) is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the *oxidation* of Zn to $Zn^{2+}$, often called the $Zn/Zn^{2+}$ *redox couple*, or the $Zn/Zn^{2+}$ *couple*, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain $E°_{cell}$: 0 − (−0.76 V) = 0.76 V.

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, *$E°$ values are independent of the stoichiometric coefficients for the half-reaction*, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

## Note the Pattern

$E°$ values do not depend on the stoichiometric coefficients for a half-reaction.

To measure the potential of the $Cu/Cu^{2+}$ couple, we can construct a galvanic cell analogous to the one shown in Figure 19.2.3 but containing a $Cu/Cu^{2+}$ couple in the sample compartment instead of $Zn/Zn^{2+}$. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the $Zn/Zn^{2+}$ couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of $Cu^{2+}$ to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and $H_2$ is oxidized to $H^+$ at the platinum electrode. In this cell, the copper strip is the *cathode*, and the hydrogen electrode is the *anode*. The cell diagram therefore is written with the SHE on the left and the $Cu^{2+}/Cu$ couple on the right:

$$Pt\,(s)\mid H_2\,(g, 1\ atm)\mid H^+\,(aq,\ 1M)\parallel Cu^{2+}\,(aq)\mid Cu\,(s)$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

$$cathode: Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s) \quad E^o_{cathode} = 0.34\ V$$

$$anode: H_2(g) \rightarrow 2H^+(aq) + 2e^- \quad E^o_{anode} = 0\ V$$

$$overall: H_2(g) + Cu^{2+}(aq) \rightarrow Cu(s) + 2H^+(aq)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.34$$

Thus the standard electrode potential for the $Cu^{2+}$/Cu couple is 0.34 V.

## Balancing Redox Reactions Using the Half-Reaction Method

In Chapter 8, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq) + H_2(g)$$

In this reaction, Al(s) is oxidized to $Al^{3+}$, and $H^+$ in water is reduced to $H_2$ gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed in Table P1, we find the corresponding half-reactions that describe the reduction of $H^+$ ions in water to $H_2$ and the oxidation of Al to $Al^{3+}$ in basic solution:

$$reduction: \ 2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$$

$$oxidation: \ Al(s) + 4OH^-(aq) \rightarrow Al(OH)_4^-(aq) + 3e^-$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 19.2.13, two $H^+$ ions gain one electron each in the reduction; in Equation 19.2.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 19.2.13) by 3 and the oxidation half-reaction (Equation 19.2.14) by 2 to give the same number of electrons in both half-reactions:

$$reduction: \ 6H_2O(l) + 6e^- \rightarrow 6OH^-(aq) + 3H_2(g)$$

$$oxidation: \ 2Al(s) + 8OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 6e^-$$

$$6H_2O(l) + 2Al(s) + 8OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 6OH^-(aq) + 3H_2(g)$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O(l) + 2Al(s) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H$$

The atoms also balance, so Equation 19.2.18 is a balanced chemical equation for the redox reaction depicted in Equation 19.20.

### Note the Pattern

The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1 but instead focus on the atoms whose oxidation states

change, as illustrated in the following steps:

**Step 1:** Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 19.213, hydrogen is reduced from $H^+$ in $OH^-$ to $H_2$, and aluminum is oxidized from $Al^0$ to $Al^{3+}$:

$$reduction:\ OH^-(aq) \rightarrow H_2(g)$$

$$oxidation:\ Al(s) \rightarrow Al(OH)_4^-(aq)$$

**Step 2:** Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding $H_2O$ and balance H atoms by adding $H^+$.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

$$reduction:\ OH^-(aq) \rightarrow H_2(g) + H_2O(l)$$

$$oxidation:\ Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq)$$

Balancing H atoms by adding $H^+$, we obtain the following:

$$reduction:\ OH^-(aq) + 3H^+(aq) \rightarrow H_2(g) + H_2O(l)$$

$$oxidation:\ Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq) + 4H^+(aq)$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

**Step 3:** Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of $H^+$ ions to $H_2$, and three electrons are lost during the oxidation of $Al^0$ to $Al^{3+}$:

$$reduction:\ OH^-(aq) + 3H^+(aq) + 2e^- \rightarrow H_2(g) + H_2O(l)$$

$$oxidation:\ Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq) + 4H^+(aq) + 3e^-$$

**Step 4:** Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 19.2.26 (the reductive half-reaction) by 3 and Equation 19.2.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

$$reduction:\ 3OH^-(aq) + 9H^+(aq) + 6e^- \rightarrow 3H_2(g) + 3H_2O(l)$$

$$oxidation:\ 2Al(s) + 8H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 8H^+(aq) + 6e^-$$

**Step 5:** Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$oxidation:\ 2Al(s) + 5H_2O(l) + 3OH^-(aq) + H^+(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

We have three $OH^-$ and one $H^+$ on the left side. Neutralizing the $H^+$ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$oxidation:\ 2Al(s) + 6H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

**Step 6:** Check to make sure that all atoms and charges are balanced.

Equation 19.2.31 is identical to Equation 19.2.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.



**Figure 19.2.4 The Reaction of Dichromate with Iodid**e The reaction of a yellow solution of sodium dichromate with a colorless solution of sodium iodide produces a deep amber solution that contains a green $Cr^{3+}$(aq) complex and brown $I_2$(aq) ions.

### Example 19.2.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide ($I^-$) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}$(aq) complex and brown $I_2$(aq) ions (Figure 19.2.4.):

$$Cr_2O_7^{2-}\,(aq) + I^-\,(aq) \rightarrow Cr^{3+}\,(aq) + 3I_2\,(aq)$$

Balance this equation using half-reactions.

**Given:** redox reaction and Table P1

**Asked for:** balanced chemical equation using half-reactions

**Strategy:**

Follow the steps to balance the redox reaction using the half-reaction method.

**Solution:**

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

$$reduction:\ Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^- \rightarrow 2Cr^{3+}\,(aq) + 7H_2O\,(l)$$

$$oxidation:\ 2I^-\,(aq) \rightarrow I_2\,(aq) + 2e^-$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

$$oxidation:\ 6I^-\,(aq) \rightarrow 3I_2\,(aq) + 6e^-$$

oxidation: $6I^-(aq) \rightarrow 3I_2(aq) + 6e^-$

Adding the two half-reactions and canceling electrons,

$$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6I^-\,(aq) \rightarrow 2Cr^{3+}\,(aq) + 7H_2O\,(l) + 3I_2\,(aq)$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$\begin{array}{cc} (-2) + 14 + (-6) & = +6 \\ +6 & = +6 \\ 2Cr + 7O + 14H + 6I & 2Cr + 7O + 14H + 6I \end{array}$$

The charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

**Step 1:** Chromium is reduced from $Cr^{6+}$ in $Cr_2O_7^{2-}$to $Cr^{3+}$, and $I^-$ ions are oxidized to $I_2$. Dividing the reaction into two half-reactions,

$$reduction:\ Cr_2O_7^{2-}\,(aq) \rightarrow Cr^{3+}\,(aq)$$

$$oxidation:\ I^-\,(aq) \rightarrow I_2\,(aq)$$

**Step 2:** Balancing the atoms other than oxygen and hydrogen,

$$reduction:\ Cr_2O_7^{2-}\,(aq) \rightarrow 2Cr^{3+}\,(aq)$$

$$oxidation:\ 2I^-\,(aq) \rightarrow I_2\,(aq)$$

We now balance the O atoms by adding $H_2O$—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

Next we balance the H atoms by adding $H^+$ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

$$reduction:\ Cr_2O_7^{2-}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + 7H_2O\,(l)$$

**Step 3:** We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to $I_2$) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

$$reduction: \ Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

**Step 4:** To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

$$oxidation: \ 6I^-(aq) \rightarrow 3I_2(aq) + 6e^-$$

**Step 5:** Adding the two half-reactions and canceling substances that appear in both reactions,

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

**Step 6:** This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

Exercise

Copper is commonly found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid ($HNO_3$), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$CuS(s) + HNO_3 \rightarrow NO(g) + CuSO_4$$

Balance this equation using the half-reaction method.

**Answer:** $3CuS(s) + 8HNO_3 \rightarrow 8NO(g) + 3CuSO_4 + 4H_2O(l)$

## Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called *voltage*. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$$

We know the values of $E°_{anode}$ for the reduction of $Zn^{2+}$ and $E°_{cathode}$ for the reduction of $Cu^{2+}$, so we can calculate $E°_{cell}$:

$$cathode: \ Cu^{2+}(aq, 1M) + 2e^- \rightarrow Cu(s) \quad E^o_{cathode} = 0.34 \ V$$

$$anode: \ Zn(s) \rightarrow Zn^{2+}(aq, 1M) + 2e^- \quad E^o_{anode} = -0.76 \ V$$

$$overall \ Zn(s) + Cu^{2+}(aq, 1M) \rightarrow Zn^{2+}(aq, 1M) + Cu(s)$$

$$E_{cell} = E^o_{cathode} - E_{anode} = 1.10 \ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction.As we shall see in Section 19.7, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

### Note the Pattern

A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.

### Example 19.2.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$cathode: \ Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$
$$anode: \ Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

If the potential for the oxidation of Ga to $Ga^{3+}$ is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to $Ni^{2+}$?

**Given:** galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

**Asked for:** standard electrode potential of reaction occurring at the cathode

**Strategy:**

**A** Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

**B** Use Equation 19.2.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

**Solution:**

**A** We have been given the potential for the oxidation of Ga to $Ga^{3+}$ under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

**B** Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of $Ni^{2+}$ to Ni from Equation 19.2.2:

$$\begin{aligned} E_{cell} &= E^o_{cathode} - E_{anode} \\ 0.27\ V &= E^o_{cathode} - (-0.55\ V) \\ E^o_{cathode} &= -0.28\ V \end{aligned}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the *oxidation* of Ni to $Ni^{2+}$ under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\ V) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are *independent* of stoichiometry.

Exercise

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $[Hg(CH_3CO_2)_2]$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

$$\begin{aligned} cathode: &\ Hg^{2+}(aq) + 2e^- \rightarrow Hg(l) \\ anode: &\ Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \end{aligned}$$

If the potential for the oxidation of Mg to $Mg^{2+}$ is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

**Answer:** 0.85 V

## Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called indicator electrodeThe electrode of a galvanic cell whose potential is related to the concentration of the substance being measured., whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the reference electrodeAn electrode in an galvanic cell whose potential is unaffected by the properties of the solution., must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

### Note the Pattern

The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the silver–silver chloride electrodeA reference electrode that consists of a silver wire coated with a very thin layer of AgCl and dipped into a chloride ion solution with a fixed concentration., which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^{-}\,(aq)\mid AgCl\,(s)\mid Ag\,(s)$$
$$AgCl\,(s)+e^{-}\rightarrow Ag\,(s)+Cl^{-}\,(aq)$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the saturated calomel electrode (SCE)A reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; <math display="inline" xml:id="av_1.0-19_m021"><semantics><mrow><msub><mrow><mtext>Hg</mtext></mrow><mn>2</mn></msub><msub><mrow><mtext>Cl</mtext></mrow><mn>2</mn></msub></mrow></semantics></math>) and KCl in an interior cell, which is surrounded by an aqueous KCl solution., which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury ($Hg_2Cl_2$; called *calomel* in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 19.2.5). Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt\,(s)\mid Hg_2Cl_2\,(s)\mid KCl\,(aq,sat)$$
$$Hg_2Cl_2\,(s)+2e^{-}\rightarrow 2Hg\,(l)+2Cl^{-}\,(aq)$$

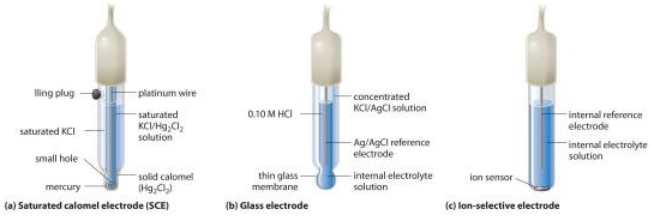



Figure 19.2.5 Three Common Types of Electrodes: (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; $Hg_2Cl_2$) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the $H^+$ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution.

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the $H^+$ ion concentration of a solution. A glass electrodeAn electrode used to measure the <math display="inline" xml:id="av_1.0-19_m022"><semantics><mrow><msup><mtext>H</mtext><mo>+</mo></msup></mrow></semantics></math> ion concentration of a solution and consisting of an internal Ag/AgCl electrode immersed in a 1 M HCl solution that is separated from the solution by a very thin glass membrane. is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 19.2.5). The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that pH = $-\log[H^+]$:

$$E_{glass} = E' + (0.0591\ V \times log\,[H^+]) = E' - 0.0591\ V \times pH$$

The voltage $E'$ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is *calibrated*; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodesAn electrode whose potential depends on only the concentration of a particular species in solution. are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 19.2.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped $LaF_3$ as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called *fluoride electrode*. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 19.2.1.

**Table 19.2.1 Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods**

| Species | Type of Sample |
|---|---|
| $H^+$ | laboratory samples, blood, soil, and ground and surface water |
| $NH_3/NH_4^+$ | wastewater and runoff water |
| $K^+$ | blood, wine, and soil |
| $CO_2/HCO_3^-$ | blood and groundwater |
| $F^-$ | groundwater, drinking water, and soil |
| $Br^-$ | grains and plant extracts |
| $I^-$ | milk and pharmaceuticals |
| $NO_3^-$ | groundwater, drinking water, soil, and fertilizer |

## Summary

The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the **standard cell potential ($E°_{cell}$)**. Only the *difference* between the potentials of two electrodes can be measured. By convention, all tabulated values of *standard electrode potentials* are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} - E°_{anode}$). The potential of the **standard hydrogen electrode (SHE)** is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its **standard electrode potential**. The standard cell potential is a measure of the driving force for a given redox reaction. All $E°$ values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of $E°$ corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an **indicator electrode** is related to the concentration of the substance being measured, whereas the potential of the **reference electrode** is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the **silver–silver chloride electrode**; the **saturated calomel electrode (SCE)**; the **glass electrode**, which is commonly used to measure pH; and **ion-selective electrodes**, which depend on the concentration of a

single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for $E°$.

## Key Takeaways

- Redox reactions can be balanced using the half-reaction method.
- The standard cell potential is a measure of the driving force for the reaction.

## Key Equation

**Standard cell potential**

Equation 19.2.2: $E°_{cell} = E°_{cathode} - E°_{anode}$

## Conceptual Problems

1. Is a hydrogen electrode chemically inert? What is the major disadvantage to using a hydrogen electrode?
2. List two factors that affect the measured potential of an electrochemical cell and explain their impact on the measurements.
3. What is the relationship between electron flow and the potential energy of valence electrons? If the valence electrons of substance A have a higher potential energy than those of substance B, what is the direction of electron flow between them in a galvanic cell?
4. If the components of a galvanic cell include aluminum and bromine, what is the predicted direction of electron flow? Why?
5. Write a cell diagram representing a cell that contains the $Ni/Ni^{2+}$ couple in one compartment and the SHE in the other compartment. What are the values of $E°_{cathode}$, $E°_{anode}$, and $E°_{cell}$?
6. Explain why $E°$ values are independent of the stoichiometric coefficients in the corresponding half-reaction.
7. Identify the oxidants and the reductants in each redox reaction.
    1. $Cr(s) + Ni^{2+}(aq) \rightarrow Cr^{2+}(aq) + Ni(s)$
    2. $Cl_2(g) + Sn^{2+}(aq) \rightarrow 2Cl^-(aq) + Sn^{4+}(aq)$
    3. $H_3AsO_4(aq) + 8H^+(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4H_2O(l) + 4Zn^{2+}(aq)$
    4. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$
8. Identify the oxidants and the reductants in each redox reaction.
    1. $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$
    2. $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$
    3. $H^+(aq) + 2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5HSO_4^-(aq)$
    4. $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$
9. All reference electrodes must conform to certain requirements. List the requirements and explain their significance.
10. For each application, describe the reference electrode you would use and explain why. In each case, how would the measured potential compare with the corresponding $E°$?
    1. measuring the potential of a $Cl^-/Cl_2$ couple
    2. measuring the pH of a solution
    3. measuring the potential of a $MnO_4-/Mn^{2+}$ couple

## Answers

1.
2.
3.
4.
5. $$Ni\,(s) \mid Ni^{2+}\,(aq) \parallel H^+\,(aq, 1\ M) \mid H_2\,(g, 1\ atm) \mid Pt\,(s)$$

| | | |
|---|---|---|
| $E^o_{anode}$ | $Ni^{2+}\,(aq) + 2e^- \rightarrow Ni\,(s)$ | $-0.257\ V$ |
| $E^o_{cathode}$ | $2H^+\,(aq) + 2e^- \rightarrow H_2\,(g,)$ | $0.000\ V$ |
| $E^o_{cell}$ | $2H^+\,(aq) + Ni\,(s) \rightarrow H_2\,(g,) + Ni^{2+}\,(aq)$ | $0.257\ V$ |

6.

7. 1. oxidant: $Ni^{2+}$(aq); reductant: Cr(s)
   2. oxidant: $Cl_2$(g); reductant: $Sn^{2+}$(aq)
   3. oxidant: $H_3AsO_4$(aq); reductant: Zn(s)
   4. oxidant: $NO_2$(g); reductant: $NO_2$(g)

8.

9.

10.

## Numerical Problems

1. Draw the cell diagram for a galvanic cell with an SHE and a copper electrode that carries out this overall reaction:

   $H_2$(g) + $Cu^{2+}$(aq) → $2H^+$(aq) + Cu(s).

2. Draw the cell diagram for a galvanic cell with an SHE and a zinc electrode that carries out this overall reaction:

   Zn(s) + $2H^+$(aq) → $Zn^{2+}$(aq) + $H_2$(g).

3. Balance each reaction and calculate the standard electrode potential for each. Be sure to include the physical state of each product and reactant.

   1. $Cl_2$(g) + $H_2$(g) → $2Cl^-$(aq) + $2H^+$(aq)
   2. $Br_2$(aq) + $Fe^{2+}$(aq) → $2Br^-$(aq) + $Fe^{3+}$(aq)
   3. $Fe^{3+}$(aq) + Cd(s) → $Fe^{2+}$(aq) + $Cd^{2+}$(aq)

4. Balance each reaction and calculate the standard reduction potential for each. Be sure to include the physical state of each product and reactant.

   1. $Cu^+$(aq) + $Ag^+$(aq) → $Cu^{2+}$(aq) + Ag(s)
   2. Sn(s) + $Fe^{3+}$(aq) → $Sn^{2+}$(aq) + $Fe^{2+}$(aq)
   3. Mg(s) + $Br_2$(l) → $2Br^-$(aq) + $Mg^{2+}$(aq)

5. Write a balanced chemical equation for each redox reaction.

   1. $H_2PO_2^-$(aq) + $SbO_2^-$(aq) → $HPO_3^{2-}$(aq) + Sb(s) in basic solution
   2. $HNO_2$(aq) + $I^-$(aq) → NO(g) + $I_2$(s) in acidic solution
   3. $N_2O$(g) + $ClO^-$(aq) → $Cl^-$(aq) + $NO_2^-$(aq) in basic solution
   4. $Br_2$(l) → $Br^-$(aq) + $BrO_3^-$(aq) in basic solution
   5. $Cl(CH_2)_2OH$(aq) + $K_2Cr_2O_7$(aq) → $ClCH_2CO_2H$(aq) + $Cr^{3+}$(aq) in acidic solution

6. Write a balanced chemical equation for each redox reaction.

   1. $I^-$(aq) + $HClO_2$(aq) → $IO_3^-$(aq) + $Cl_2$(g) in acidic solution
   2. $Cr^{2+}$(aq) + $O_2$(g) → $Cr^{3+}$(aq) + $H_2O$(l) in acidic solution
   3. $CrO_2^-$(aq) + $ClO^-$(aq) → $CrO_4^{2-}$(aq) + $Cl^-$(aq) in basic solution
   4. S(s) + $HNO_2$(aq) → $H_2SO_3$(aq) + $N_2O$(g) in acidic solution
   5. $F(CH_2)_2OH$(aq) + $K_2Cr_2O_7$(aq) → $FCH_2CO_2H$(aq) + $Cr^{3+}$(aq) in acidic solution

7. The standard cell potential for the oxidation of Pb to $Pb^{2+}$ with the concomitant reduction of $Cu^+$ to Cu is 0.39 V. You know that $E°$ for the $Pb^{2+}$/Pb couple is −0.13 V. What is $E°$ for the $Cu^+$/Cu couple?

8. You have built a galvanic cell similar to the one in Figure 19.2.3 using an iron nail, a solution of $FeCl_2$, and an SHE. When the cell is connected, you notice that the iron nail begins to corrode. What else do you observe? Under standard conditions, what is $E_{cell}$?

9. Carbon is used to reduce iron ore to metallic iron. The overall reaction is as follows:

$$2Fe_2O_3{\cdot}xH_2O(s) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g) + 2xH_2O(g)$$

Write the two half-reactions for this overall reaction.

10. Will each reaction occur spontaneously under standard conditions?
    1. $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$
    2. $Zn^{2+}(aq) + Pb(s) \rightarrow Zn(s) + Pb^{2+}(aq)$
11. Each reaction takes place in acidic solution. Balance each reaction and then determine whether it occurs spontaneously as written under standard conditions.
    1. $Se(s) + Br_2(l) \rightarrow H_2SeO_3(aq) + Br^-(aq)$
    2. $NO_3^-(aq) + S(s) \rightarrow HNO_2(aq) + H_2SO_3(aq)$
    3. $Fe^{3+}(aq) + Cr^{3+}(aq) \rightarrow Fe^{2+}(aq) + Cr_2O_7^{2-}(aq)$
12. Calculate $E°_{cell}$ and $\Delta G°$ for the redox reaction represented by the cell diagram $Pt(s)\,|\,Cl_2(g, 1\ atm)\,\|\,ZnCl_2(aq, 1\ M)\,|\,Zn(s)$. Will this reaction occur spontaneously?
13. If you place Zn-coated (galvanized) tacks in a glass and add an aqueous solution of iodine, the brown color of the iodine solution fades to a pale yellow. What has happened? Write the two half-reactions and the overall balanced chemical equation for this reaction. What is $E°_{cell}$?
14. Your lab partner wants to recover solid silver from silver chloride by using a 1.0 M solution of HCl and 1 atm $H_2$ under standard conditions. Will this plan work?

## Answers

1. $Pt(s)\,|\,H_2(g, 1\ atm)\,|\,H^+(aq, 1M)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$
2. 
3. 
    1. $Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)$; $E° = 1.358$ V
    2. $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$; $E° = 0.316$ V
    3. $2Fe^{3+}(aq) + Cd(s) \rightarrow 2Fe^{2+}(aq) + Cd^{2+}(aq)$; $E° = 1.174$ V
4. 
5. 
6. 
7. 
8. 
9. 
10. 
11. 
12. 
13. 
14. 

## Contributors

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# 19.4: Comparing Strengths of Oxidants and Reductants

**Learning Objectives**

- To know how to predict the relative strengths of various oxidants and reductants.

We can use the procedure described in Section 19.2 to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table 19.3.1 (Table P1 contains a more extensive listing.) These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 19.3.1 . All reactants that lie *above* the SHE in the table are stronger oxidants than $H^+$, and all those that lie below the SHE are weaker. The strongest oxidant in the table is $F_2$, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

**Table 19.3.1 Standard Potentials for Selected Reduction Half-Reactions at 25°C**


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| Half-Reaction | $E°$ (V) |
|---|---|
| $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ | 2.87 |
| $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$ | 1.78 |
| $Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$ | 1.72 |
| $PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ | 1.69 |
| $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ | 1.36 |
| $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ | 1.23 |
| $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ | 1.23 |
| $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$ | 1.22 |
| $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ | 1.09 |
| $NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$ | 0.93 |
| $Ag^+(aq) + e^- \rightarrow Ag(s)$ | 0.80 |
| $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ | 0.77 |
| $H_2SeO_3(aq) + 4H^+ + 4e^- \rightarrow Se(s) + 3H_2O(l)$ | 0.74 |
| $O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$ | 0.70 |
| $MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$ | 0.60 |
| $MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightarrow MnO_2(s) + 4OH^-(aq)$ | 0.60 |
| $I_2(s) + 2e^- \rightarrow 2I^-(aq)$ | 0.54 |
| $H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightarrow S(s) + 3H_2O(l)$ | 0.45 |
| $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ | 0.40 |
| $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ | 0.34 |
| $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ | 0.22 |
| $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ | 0.15 |
| $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ | 0.15 |
| $2H^+(aq) + 2e^- \rightarrow H_2(g)$ | 0.00 |
| $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ | −0.14 |
| $2SO_4^{2-}(aq) + 4H+(aq) + 2e^- \rightarrow S_2O_6^{2-}(aq) + 2H_2O(l)$ | −0.22 |
| $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ | −0.26 |
| $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$ | −0.36 |
| $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ | −0.40 |
| $Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$ | −0.41 |
| $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ | −0.45 |
| $Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$ | −0.69 |
| $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ | −0.76 |

| Half-Reaction | $E°$ (V) |
|---|---|
| $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ | −1.662 |
| $Be^{2+}(aq) + 2e^- \rightarrow Be(s)$ | −1.85 |
| $Li^+(aq) + e^- \rightarrow Li(s)$ | −3.04 |

Similarly, all species in Table 19.3.1 that lie *below* $H_2$ are stronger reductants than $H_2$, and those that lie above $H_2$ are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of −3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the $Li^+$ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{hydration}$ for $Li^+$ compared with $Cs^+$. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

## Note the Pattern

Species in Table 19.3.1 that lie below $H_2$ are stronger reductants (more easily oxidized) than $H_2$. Species that lie above $H_2$ are stronger oxidants.

Because the half-reactions shown in Table 19.3.1 are arranged in order of their $E°$ values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies *below* it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies *above* it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{cell} > 0$), as illustrated in Example 5.



## Example 19.3.1

The black tarnish that forms on silver objects is primarily $Ag_2S$. The half-reaction for reversing the tarnishing process is as follows:

$$Ag_2S\,(s) + 2e^- \rightarrow 2Ag\,(s) + S^{2-}\,(aq) \quad E^o = -0.69\ V$$

1. Referring to Table 19.3.1 , predict which species—$H_2O_2$(aq), Zn(s), $I^-$(aq), $Sn^{2+}$(aq)—can reduce $Ag_2S$ to Ag under standard conditions.
2. Of these species—$H_2O_2$(aq), Zn(s), $I^-$(aq), $Sn^{2+}$(aq), identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.
3. From the data in Table 19.3.1 , suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.

**Given:** reduction half-reaction, standard electrode potential, and list of possible reductants

**Asked for:** reductants for $Ag_2S$, strongest reductant, and potential reducing agent for removing tarnish

**Strategy:**

**A** From their positions in Table 19.3.1, decide which species can reduce $Ag_2S$. Determine which species is the strongest reductant.

**B** Use Table 19.3.1 to identify a reductant for $Ag_2S$ that is a common household product.

**Solution:**

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the $Ag_2S/Ag$ couple in Table 19.3.1 or (2) compare $E°$ for each species with $E°$ for the $Ag_2S/Ag$ couple (−0.69 V).

1. **A** The species in Table 19.3.1 are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ lie above $Ag_2S$, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce $Ag_2S(s)$ under standard conditions, whereas $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ cannot. $Sn^{2+}(aq)$ and $H_2O_2(aq)$ appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.
2. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table 19.3.1 than the half-reactions involving $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$. (Commercial products that use a piece of zinc are often marketed as a "miracle product" for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)
3. **B** Of the reductants that lie below Zn(s) in Table 19.3.1 , and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

Exercise

Refer to Table 19.3.1 to predict

1. which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—can oxidize $MnO_2(s)$ to $MNO_4^-$ under standard conditions.
2. which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—is the strongest oxidizing agent in aqueous solution.

**Answer**

1. $Ag^+(aq)$; $H_2O_2(aq)$
2. $H_2O_2(aq)$

## Example 19.3.2

Use the data in Table 19.3.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)$
2. $MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)$

**Given:** redox reaction and list of standard electrode potentials (Table 19.3.1)

**Asked for:** reaction spontaneity

**Strategy:**

**A** Identify the half-reactions in each equation. Using Table 19.3.1, determine the standard potentials for the half-reactions in the appropriate direction.

**B** Use Equation 19.2.2 to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

**Solution:**

1. **A** Metallic tin is oxidized to $Sn^{2+}(aq)$, and $Be^{2+}(aq)$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (−1.85 V) and for the former (oxidation) half-reaction (−0.14 V) directly from Table 19.3.1.

   **B** Adding the two half-reactions gives the overall reaction:

$$\begin{array}{lcc} cathode: & MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) & E^o_{cathode} = 1.22\ V \\ anode: & H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^- & E^o_{anode} = 1.22\ V \\ overall: & MnO_2(s) + 2H^+(aq) + H_2O_2(aq) \rightarrow & E^o_{cell} = E^o_{cathode} - E^o_{anode} \\ & O_2(g) + Mn^{2+}(aq) + 2H_2O(l) & -0.53\ V \end{array}$$

   The standard cell potential is quite negative, so the reaction will *not* occur spontaneously as written. That is, metallic tin cannot be used to reduce $Be^{2+}$ to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions ($Sn^{2+}$) by metallic beryllium, which has a positive value of $E°_{cell}$, will occur spontaneously.

2. **A** $MnO_2$ is the oxidant ($Mn^{4+}$ is reduced to $Mn^{2+}$), while $H_2O_2$ is the reductant ($O^{2-}$ is oxidized to $O_2$). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from Table 19.2.

   **B** The two half-reactions and their corresponding potentials are as follows:

$$\begin{array}{lcc} cathode: & MnO_2\,(s) + 4H^+\,(aq) + 2e^- \rightarrow Mn^{2+}\,(aq) + 2H_2O\,(l) & E^o_{cathode} = 1.22\ V \\ anode: & H_2O_2\,(aq) \rightarrow O_2\,(g) + 2H^+\,(aq) + 2e^- & E^o_{anode} = 1.22\ V \\ overall: & MnO_2\,(s) + 2H^+\,(aq) + H_2O_2\,(aq) \rightarrow & E^o_{cell} = E^o_{cathode} - E^o_{anode} \\ & O_2\,(g) + Mn^{2+}\,(aq) + 2H_2O\,(l) & -0.53\ V \end{array}$$

   The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce $MnO_2$, and oxygen gas will evolve from the solution.

Exercise

Use the data in Table 19.3.2 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $2Ce^{4+}(aq) + 2Cl^-(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g)$
2. $4MnO_2(s) + 3O_2(g) + 4OH^-(aq) \rightarrow 4MnO_4^-(aq) + 2H_2O$

**Answer**

1. spontaneous ($E°_{cell}$ = 0.36 V)
2. nonspontaneous ($E°_{cell}$ = −0.20 V)

Although the sign of $E°_{cell}$ tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what *extent* the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics, as described in Section 19.4.

## Summary

The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong intermolecular electrostatic interactions, and not in the gas phase.

## Key Takeaway

- The relative strengths of various oxidants and reductants can be predicted using $E°$ values.

## Conceptual Problems

1. The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?
2. Without referring to tabulated data, of $Br_2/Br^-$, $Ca^{2+}/Ca$, $O_2/OH^-$, and $Al^{3+}/Al$, which would you expect to have the *least* negative electrode potential and which the *most* negative? Why?
3. Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($H_2C_2O_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?
4. The electrode potential for the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to −0.34/2 V? Explain your answer.

## Answer

1.
2.
3. No; $E°$ = −0.691 V for $Ag_2S(s) + 2e^- \rightarrow Ag(s) + S^{2-}(aq)$, which is too negative for $Ag_2S$ to be spontaneously reduced by oxalic acid [$E°$ = 0.49 V for $2CO_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2C_2O_4(aq)$]

4.

## Contributors

- Anonymous

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# 19.5: Electrochemical Cells and Thermodynamics

**Learning Objectives**

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with $Ni^{2+}$(aq) to form Ni(s) and $Co^{2+}$(aq) occurs spontaneously, but if we reduce the concentration of $Ni^{2+}$ by a factor of 100, so that [$Ni^{2+}$] is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

## The Relationship between Cell Potential and Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in coulombs (C)The SI unit of measure for the number of electrons that pass a given point in 1 second; it is defined as $6.25\times10^{18}$ $e^-$/s and relates electron potential (in volts) to energy (in joules): 1 J/1 V = 1 C., an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in amperes (A)The fundamental SI unit of electric current; it is defined as the flow of 1 C/s past a given point: 1A = 1 C/s.; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ J}{1\ V} = 1\ C = 1\ A \cdot s$$

In chemical reactions, however, we need to relate the coulomb to the charge on a *mole* of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the faraday (*F*)The charge on 1 mol of electrons; it is obtained by multiplying the charge on the electron by Avogadro's number., named after the English physicist and chemist Michael Faraday (1791–1867):

$$F = \left(1.60218 \times 10^{-19}\ C\right) \frac{6.02214 \times 10^{23}}{1\ mole}$$

$$F = 9.64855 \times 10^{4}\ C/mole \simeq 96,486 C/\left(mol\ e^{-}\right)$$

The total charge transferred from the reductant to the oxidant is therefore *nF*, where *n* is the number of moles of electrons.

### Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell ($w_{max}$) is equal to the product of the cell potential ($E_{cell}$) and the total charge transferred during the reaction (*nF*):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done *by* a system (an electrochemical cell with a positive potential) *on* its surroundings.

As you learned in Chapter 18, the change in free energy ($\Delta G$) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and $\Delta G$, the most important thermodynamic quantity discussed in Chapter 18. This relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a *negative* value of $\Delta G$ and a *positive* value of $E_{cell}$, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between $\Delta G°$ and $E°_{cell}$ is as follows:

$$\Delta G^o = -nFE^o_{cell}$$

### Note the Pattern

A spontaneous redox reaction is characterized by a negative value of $\Delta G°$, which corresponds to a positive value of $E°_{cell}$.

### Example 19.4.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table 19.3.1, calculate the free-energy change ($\Delta G°$) for this redox reaction under standard conditions. Is the reaction spontaneous?

**Given:** redox reaction

**Asked for:** $\Delta G°$ for the reaction and spontaneity

**Strategy:**

**A** From the relevant half-reactions and the corresponding values of $E°$, write the overall reaction and calculate $E°_{cell}$ using Equation 19.2.2.

**B** Determine the number of electrons transferred in the overall reaction. Then use Equation 19.4.5 to calculate $\Delta G°$. If $\Delta G°$ is negative, then the reaction is spontaneous.

**Solution:**

**A** As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of $E°$. From Table 19.3.1, we can find the reduction and oxidation half-reactions and corresponding $E°$ values:

$$\begin{array}{lll} cathode: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^o_{cathode} = 1.23\ V \\ anode: & 2Br^-(aq) \rightarrow Br_2(aq) + 2e^- & E^o_{anode} = 1.09\ V \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of $E°$ is not affected:

$$\begin{array}{lll} cathode: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^o_{cathode} = 1.23\ V \\ anode: & 6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^- & E^o_{anode} = 1.09\ V \\ overall: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6BrI^- \rightarrow & E^o_{cell} = 0.14\ V \\ & 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(aq) & \end{array}$$

**B** We can now calculate $\Delta G°$ using Equation 19.4.10 Because six electrons are transferred in the overall reaction, the value of $n$ is 6:

$$\Delta G^o = -nFE^o_{cell} = \left(6\ \cancel{mol}\right)\left(96,468\ J/\left(\cancel{V}\cdot\cancel{mol}\right)\right)\left(0.14\ \cancel{V}\right)$$

$$-8.1 \times 10^4\ J$$

$$-81\ kJ/mol\ Cr_2O_7$$

Thus $\Delta G°$ is −81 kJ for the reaction as written, and the reaction is spontaneous.

Exercise

Use the data in Table 19.3.1 to calculate $\Delta G°$ for the reduction of ferric ion by iodide:

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$

Is the reaction spontaneous?

**Answer:** −44 kJ/mol $I_2$; yes

## Potentials for the Sums of Half-Reactions

Although Table 19.3.1 and Table P1 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $Fe^{3+}$(aq) to Fe(s) is not listed in the table, but two related reductions are given:

$$Fe^{3+}\,(aq) + e^- \rightarrow Fe^{2+}\,(aq) \quad E^o = 0.77\ V$$

$$Fe^{2+}\,(aq) + 2e^- \rightarrow Fe\,(aq) \quad E^o = -0.45\ V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction *because E° is not a state function*. However, because Δ*G*° is a state function, the sum of the Δ*G*° values for the individual reactions gives us Δ*G*° for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (*n*) transferred. To obtain the value of *E*° for the overall half-reaction, we first must add the values of Δ*G*° (= −*nFE*°) for each individual half-reaction to obtain Δ*G*° for the overall half-reaction:

$$Fe^{3+}\,(aq) + e^- \rightarrow \cancel{Fe^{2+}\,(aq)} \quad \Delta G^o = (-1)\,F\,(0.77\ V) \tag{19.4.8}$$

$$\cancel{Fe^{2+}\,(aq)} + 2e^- \rightarrow Fe\,(s) \quad \Delta G^o = (-2)\,F\,(-0.457\ V)$$

$$Fe^{3+}\,(aq) + e^- \rightarrow Fe\,(s) \quad \Delta G^o = (-1)\,F\,(0.77\ V) + (-2)\,F\,(-0.457\ V)$$

Solving the last expression for Δ*G*° for the overall half-reaction,

$$\Delta G^o = F\,[(-0.77\ V) + (-2)\,(-0.457\ V)] = F\,(0.13\ V)$$

Three electrons (*n* = 3) are transferred in the overall reaction (Equation 19.4.15), so substituting into Equation 19.4.10 and solving for *E*° gives the following:

$$\Delta G^o = -nFE^o_{cell}$$

$$F\,(0.13\ V) = -3FE^o_{cell}$$

$$E^o_{cell} = -\frac{0.13\ V}{3} = -0.043\ V$$

This value of *E*° is *very* different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

### Note the Pattern

Values of *E*° for half-reactions cannot be added to give *E*° for the sum of the half-reactions; only values of Δ*G*° = −*nFE*°$_{\text{cell}}$ for half-reactions can be added.

## The Relationship between Cell Potential and the Equilibrium Constant

We can use the relationship between Δ*G*° and the equilibrium constant *K*, defined in Chapter 18, to obtain a relationship between *E*°$_{\text{cell}}$ and *K*. Recall that for a general reaction of the type *a*A + *b*B → *c*C + *d*D, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^o = -RTln\ K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 19.4.9), we can write

$$-nFE^o_{cell} = -RTln\ K$$

Rearranging this equation,

$$E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ K$$

For *T* = 298 K, Equation 19.4.12 can be simplified as follows:

$$E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ K = \left[\frac{8.314\ \cancel{J}/\left(\cancel{mol}\cdot\cancel{K}\right)\left(298\ \cancel{K}\right)}{n\left[96,486\ \cancel{J}/\left(V\cdot\cancel{mol}\right)\right]}\right] 2.303\ log\ K = \left(\frac{0.0591}{n}\right) log\ K$$

Thus $E°_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of $E°_{cell}$ and vice versa.

### Example 19.4.2

Use the data in Table 19.3.1 to calculate the equilibrium constant for the reaction of metallic lead with $PbO_2$ in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

**Given:** redox reaction

**Asked for:** $K$

**Strategy:**

**A** Write the relevant half-reactions and potentials. From these, obtain the overall reaction and $E°_{cell}$.

**B** Determine the number of electrons transferred in the overall reaction. Use Equation 19.4.13 to solve for log $K$ and then $K$.

**Solution:**

**A** The relevant half-reactions and potentials from Table 19.3.1 are as follows:

$$\begin{array}{rcl} cathode: & PbO_2\left(s\right) + SO_4^{2-}\left(aq\right) + 4H^+\left(aq\right) + 2e^- \rightarrow PbSO_4\left(s\right) + 2H_2O\left(l\right) & E^o_{cathode} = 1.69\ V \\ anode: & Pb\left(s\right) + SO_4^{2-}\left(aq\right) \rightarrow PbSO_4\left(s\right) + 2e^- & E^o_{anode} = 0.36\ V \\ overall: & Pb\left(s\right)PbO_2\left(s\right) + 2SO_4^{2-}\left(aq\right) + 4H^+\left(aq\right) \rightarrow 2PbSO_4\left(s\right) + 2H_2O\left(l\right) & E^o_{cell} = 2.05\ V \end{array}$$

**B** Two electrons are transferred in the overall reaction, so $n$ = 2. Solving Equation 19.4.13 for log $K$ and inserting the values of $n$ and $E°$,

$$ln\ K = \frac{nE^o}{0.0591\ V} = \frac{2\left(2.05\ \cancel{V}\right)}{0.0591\ \cancel{V}} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

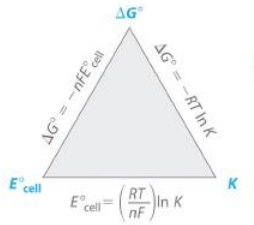
Exercise

Use the data in Table 19.3.1 to calculate the equilibrium constant for the reaction of $Sn^{2+}$(aq) with oxygen to produce $Sn^{4+}$(aq) and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}\left(aq\right) + O_2\left(g\right) + 4H^+\left(aq\right) \rightleftharpoons 2Sn^{4+}\left(aq\right) + 2H_2O\left(l\right)$$

**Answer:** $1.2 \times 10^{73}$

Figure 19.4.1 summarizes the relationships that we have developed based on properties of the *system*—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G° < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between $\Delta G$ and the reaction quotient $Q$ developed in Chapter 18 .




| ΔG° | $E^\circ_{cell}$ | K | Direction of Reaction |
|---|---|---|---|
| < 0 | > 0 | > 1 | spontaneous in forward direction |
| > 0 | < 0 | < 1 | spontaneous in reverse direction |
| 0 | 0 | 1 | no net reaction: system at equilibrium |

Figure 19.4.1 The Relationships among Criteria for Thermodynamic **Spontaneity**The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are $K$, $\Delta G^\circ$, and $E^\circ_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of $\Delta G^\circ$ and $E^\circ_{cell}$ and the magnitude of $K$ determine the direction of spontaneous reaction under standard conditions.

## The Effect of Concentration on Cell Potential: The Nernst Equation

Recall from Chapter 18 that the *actual* free-energy change for a reaction under nonstandard conditions, $\Delta G$, is given as follows:

$$\Delta G = \Delta G^o + RT\ ln\ Q$$

We also know that $\Delta G = -nFE_{cell}$ and $\Delta G^\circ = -nFE^\circ_{cell}$. Substituting these expressions into Equation 19.4.14, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT\ ln\ Q$$

Dividing both sides of this equation by $-nF$,

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ ln\ Q$$

Equation 19.4.16 is called the Nernst equationAn equation for calculating cell potentials $E_{cell}$ under nonstandard conditions; it can be used to determine the direction of spontaneous reaction for any redox reaction under an conditions:$E_{cell}$=</mo><msubsup><mi>E°−(RT/nF)lnQ, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), Equation 19.4.16 reduces to Equation 19.4.12 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

Substituting the values of the constants into Equation 19.4.16 with $T$ = 298 K and converting to base-10 logarithms give the relationship of the actual cell potential ($E_{cell}$), the standard cell potential ($E^\circ_{cell}$), and the reactant and product concentrations at room temperature (contained in $Q$):

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ ln\ Q$$

### Note the Pattern

The Nernst equation can be used to determine the value of $E_{cell}$, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 19.4.17 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 19.4.17 that the cell potential changes by 0.0591/$n$ V for each 10-fold change in the value of $Q$ because log 10 = 1.

### Example 19.4.3

In the exercise in Example 6, you determined that the following reaction proceeds spontaneously under standard conditions because $E^\circ_{cell} > 0$ (which you now know means that $\Delta G^\circ < 0$):

$$2Ce^{4+}\,(aq) + 2Cl^-\,(aq) \rightarrow 2Ce^{3+}\,(aq) + Cl_2\,(g)$$

Calculate $E$ for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}]$ = 0.013 M, $[Ce^{3+}]$ = 0.60 M, $[Cl^-]$ = 0.0030 M, $Cl_2$= 1.0 atm, and $T$ = 25°C.

**Given:** balanced redox reaction, standard cell potential, and nonstandard conditions

**Asked for:** cell potential

**Strategy:**

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

**Solution:**

We can use the information given and the Nernst equation to calculate $E_{cell}$. Moreover, because the temperature is 25°C (298 K), we can use Equation 19.4.17 instead of 19.46. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}(aq) + 2e^- \rightarrow 2Ce^{3+}(aq)$$

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

so $n = 2$. Substituting the concentrations given in the problem, the partial pressure of $Cl_2$, and the value of $E°_{cell}$ into Equation 19.4.17,

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ log\ Q$$

$$= 0.25\ V - \frac{0.0591\ V}{2}\ logn\ \left(\frac{[Ce^{3+}]^2\ P_{Cl_2}}{[Ce^{4+}]^2\ [Cl^-]^2}\right)$$

$$= 0.25\ V - [(0.0296\ V)\ (8.37)] = 0.00\ V$$

Thus the reaction will *not* occur spontaneously under these conditions (because $E = 0$ V and $\Delta G = 0$). The composition specified is that of an equilibrium mixture.

Exercise

In the exercise in Example 6, you determined that molecular oxygen will not oxidize $MnO_2$ to permanganate via the reaction

$$4MnO_2\ (s) + 3O_2\ (g) + 4OH^-\ (aq) \rightarrow 4MnO_4^-\ (aq) + 2H_2O\ (l)\ \;\;\;\ E_{cell}^{o}=-0.20\;V$$

Calculate $E_{cell}$ for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, $P(O_2) = 0.20$ atm, $[MNO_4^-] = 1.0 \times 10^{-4}$ M, and $T = 25$°C.

**Answer:** $E_{cell} = -0.22$ V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell discussed in Section 19.2 allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)\ \;\;\;\ E_{cell}^{o}=1.10\;V\ \tag{19.4.18}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M $Cu^{2+}$ and $1.0 \times 10^{-6}$ M $Zn^{2+}$. The initial voltage measured when the cell is connected can then be calculated from Equation 19.4.17:

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\ V - \frac{0.0591\ V}{2}\ log\frac{1.0 \times 10^{-6}}{1.0} = 1.28\ V$$

Thus the initial voltage is *greater* than $E°$ because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so $Q = 1$ and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of $Q$ will increase further, leading to a further decrease in $E_{cell}$. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M $Zn^{2+}$ and $1.0 \times 10^{-6}$ M $Cu^{2+}$), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V.

The variation of $E_{cell}$ with log $Q$ over this range is linear with a slope of $-0.0591/n$, as illustrated in Figure 19.4.2. As the reaction proceeds still further, $Q$ continues to increase, and $E_{cell}$ continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of $Q$ when $E_{cell} = 0$ is calculated as follows:

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ log\ Q = 0$$

$$E^o = \frac{0.0591\ V}{n}\ log\ Q$$

$$log\ Q) = \frac{E^o\ n}{0.0591\ V} = \frac{\left(1.10\ \cancel{V}\right)(2)}{0.0591\ \cancel{V}} = 37.23$$

$$Q = 10^{37.23} = 1.7 \times 10^{37}$$

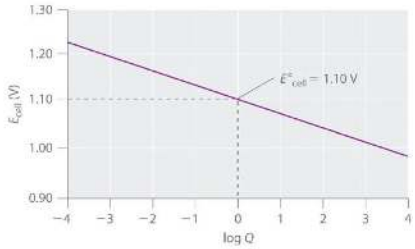



Figure 19.4.2 The Variation of $E_{cell}$ with Log $Q$ for a Zn/Cu **Cell** Initially, log $Q$ < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log $Q$ increases, and $E_{cell}$ decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log $Q$ = 0 and $E_{cell} = E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log $Q$ will increase until $Q = K$ and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with $Cu^{2+}$ to give Cu metal and $Zn^{2+}$ is $1.7 \times 10^{37}$ at 25°C.

## Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$Ag\,(s)\ |\ Ag^+\,(aq,\ 0.010\ M)\ \|\ Ag^+\,(aq,\ 1.0\ M)\ |\ Ag\,(s)$$

$$cathode:\quad Ag^+\,(aq,\ 1.0\ M) + e^- \rightarrow Ag\,(s)$$

$$anode:\quad Ag\,(s) \rightarrow Ag^+\,(aq,\ 0.010\ M) + e^-$$

$$overall:\quad Ag^+\,(aq,\ 1.0\ M) \rightarrow Ag^+\,(aq,\ 0.010\ M)$$

As the reaction progresses, the concentration of $Ag^+$ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the $Ag^+$ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The *total* mass of Ag(s) in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ logQ = 0 - \left(\frac{0.0591\ V}{1}\right) log\frac{0.010}{1.0} = 0.12$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a concentration cellAn electrochemical cell in which the anode and the cathode compartments are identical except for the concentration of a reactant.. As the reaction proceeds, the difference between the concentrations of $Ag^+$ in the two compartments will decrease, as will $E_{cell}$. Finally, when the concentration of $Ag^+$ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell}$ = 0).

### Example 19.4.4

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a $5.2 \times 10^{-2}$ M solution of $MnSO_4$ as the anode ($T$ = 25°C).

**Given:** galvanic cell, identities of the electrodes, and solution concentrations

**Asked for:** voltage

**Strategy:**

**A** Write the overall reaction that occurs in the cell.

**B** Determine the number of electrons transferr

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ log\ Q = 0 - \left(\frac{0.0591\ V}{2}\right) log \frac{5.2 \times 10^{-2}}{2.0} = 0.047$$

ed. Substitute this value into the Nernst equation to calculate the voltage.

**Solution:**

**A** This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions ($Cl^-$ and $SO_4^{2-}$) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$Mn^{2+}(aq, 2.0\ M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\ M)$

**B** For the reduction of $Mn^{2+}(aq)$ to Mn(s), $n = 2$. We substitute this value and the given $Mn^{2+}$ concentrations into Equation 19.4.17:

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

Exercise

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of $Na_2SO_4$ at pH 7.00. Both cells are in contact with the atmosphere, with $P(O_2) = 0.20$ atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$, what will be the potential when the circuit is closed?

**Answer:** 0.41 V

## Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products ($K_{sp}$) of sparingly soluble substances. As you learned in Chapter 17, solubility products can be very small, with values of less than or equal to $10^{-30}$. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 19.4.3, which is designed to measure the solubility product of silver chloride: $K_{sp} = [Ag^+][Cl^-]$. In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of $Ag^+$; the other compartment contains a silver wire inserted into a 1.0 M $Cl^-$ solution saturated with AgCl. In this system, the $Ag^+$ ion concentration in the first compartment equals $K_{sp}$. We can see this by dividing both sides of the equation for $K_{sp}$ by $[Cl^-]$ and substituting: $[Ag^+] = K_{sp}/[Cl^-] = K_{sp}/1.0 = K_{sp}$. The overall cell reaction is as follows:

$Ag^+(aq, concentrated) \rightarrow Ag^+(aq, dilute)$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$E_{cell} = 0 - \left(\frac{0.0591\ V}{1}\right) log \left(\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}\right) = -0.0591\ V\ log \left(\frac{K_{sp}}{1.0}\right) = -0.0591\ V$$

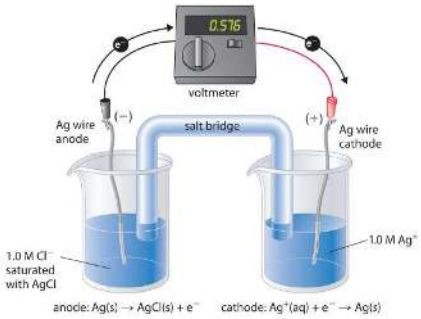



Figure 19.4.3. A Galvanic Cell for Measuring the Solubility Product of AgCl One compartment contains a silver wire inserted into a 1.0 M solution of $Ag^+$, and the other compartment contains a silver wire inserted into a 1.0 M $Cl^-$ solution saturated with AgCl. The potential due to the difference in [$Ag^+$] between the two cells can be used to determine $K_{sp}$.

By closing the circuit, we can measure the potential caused by the difference in [$Ag^+$] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 19.4.26 for $K_{sp}$,

$$log\ K_{sp} = \frac{-E_{cell}}{0.0591\ V} = \frac{-0.580\ \cancel{V}}{0.0591\ \cancel{V}} = -9.81$$

$$K_{sp} = 1.5 \times 10^{-10}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

## Example 19.4.5

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 19.4.3, which contains a 1.0 M solution of a very soluble $Pb^{2+}$ salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of $Na_2SO_4$ saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is $K_{sp}$ for $PbSO_4$? Report your answer to two significant figures.

**Given:** galvanic cell, solution concentrations, electrodes, and voltage

**Asked for:** $K_{sp}$

**Strategy:**

**A** From the information given, write the equation for $K_{sp}$. Express this equation in terms of the concentration of $Pb^{2+}$.

**B** Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation 19.4.26 and solve for $K_{sp}$.

**Solution:**

**A** You have constructed a concentration cell, with one compartment containing a 1.0 M solution of $Pb^{2+}$ and the other containing a dilute solution of $Pb^{2+}$ in 1.0 M $Na_2SO_4$. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of $Pb^{2+}$ in the dilute solution to $K_{sp}$:

$$\left[Pb^{2+}\right]\left[SO_4^{2-}\right] = K_{sp} \tag{19.5.1}$$

$$\left[Pb^{2+}\right] = \frac{K_{sp}}{\left[SO_4^{2-}\right]} = \frac{K_{sp}}{1.0\ M} = K_{sp} \tag{19.5.2}$$

**B** The reduction of $Pb^{2+}$ to Pb is a two-electron process and proceeds according to the following reaction:

$Pb^{2+}$(aq, concentrated) → $Pb^{2+}$(aq, dilute)

so

\( E_{cell} =E_{cell}^{o}-\dfrac{0.0591\;V}{n}\;log \;Q =

$$0.230\ V = 0 - \left(\frac{0.0591\ V}{2}\right) log\left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V\ log\left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = log\ K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise

A concentration cell similar to the one described in Example 11 contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with $LaF_3$ in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the $K_{sp}$ for $LaF_3$? Report your answer to two significant figures.

**Answer:** $5.7 \times 10^{-17}$

## Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 11, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to $K_{sp}$. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated in Example 12.

### Example 19.4.6

Suppose a galvanic cell is constructed with a standard $Zn/Zn^{2+}$ couple in one compartment and a modified hydrogen electrode in the second compartment (Figure 19.4.3). The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$Zn(s)\,|\,Zn^{2+}(aq, 1.0\ M)\,\|\,H^+(aq, ?\ M)\,|\,H_2(g, 1.0\ atm)\,|\,Pt(s)$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

**Given:** galvanic cell, cell diagram, and cell potential

**Asked for:** pH of the solution

**Strategy:**

**A** Write the overall cell reaction.

**B** Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

**Solution:**

**A** Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give $H_2$ (note that Zn lies below $H_2$ in Table 19.3.1):

$$Zn\,(s) + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g) \quad E_o = 0.76\ V$$

**B** By substituting the given values into the simplified Nernst equation (Equation 19.64), we can calculate $[H^+]$ under nonstandard conditions:

\( E_{cell} =E_{cell}^{o}-\dfrac{0.0591\;V}{n}\;log \left ( \dfrac{\left [ Zn^{2+} \right ]P_{H_{2}}}{\left [ H^{+} \right ]^{2}} \right )

$$0.26\ V = 0.76\ V - \left(\frac{0.0591\ V}{2}\right) log\left(\frac{(1.0)\,(1.0)}{[H^+]^2}\right) = -0.0296\ V\ log\left(\frac{K_{sp}}{1.0}\right)$$

$$16.9 = log\left(\frac{1}{[H^+]^2}\right) = log\,[H^+]^{-2} = -2\ log\,[H^+]$$

$$8.46 = -log\,[H^+]$$

$$8.5 = pH$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of $Pb^{2+}$ in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows"

$Pb(s)\,|\,Pb^{2+}(aq, ?\ M)\|H^{+}(aq), 1.0\ M\,|\,O_2(g, 1.0\ atm)\,|\,Pt(s)$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table 19.7.1 and Table T1 to determine the concentration of $Pb^{2+}$ in the groundwater.

**Answer:** $1.2 \times 10^{-9}$ M

## Summary

A **coulomb (C)** relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in **amperes (A)**, where 1 A is defined as the flow of 1 C/s past a given point. The **faraday (*F*)** is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the Δ*G* values for the half-reactions gives Δ*G* for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (*n*) transferred. Spontaneous redox reactions have a negative Δ*G* and therefore a positive $E_{cell}$. Because the equilibrium constant *K* is related to Δ*G*, $E°_{cell}$ and *K* are also related. Large equilibrium constants correspond to large positive values of *E*°. The **Nernst equation** allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. **Concentration cells** consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because Δ*G* = 0 at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

## Key Takeaway

- The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution.

## Key Equations

**Charge on a mole of electrons (faraday)**

Equation 19.4.2: $F \approx 96{,}486$ J/(V·mol)

**Maximum work from an electrochemical cell**

Equation 19.4.3: $w_{max} = -nFE_{cell}$

**Relationship between Δ *G* ° and Δ *E* °**

Equation 19.4.5: $\Delta G° = -nFE°_{cell}$

**Relationship between Δ *G* ° and *K* for a redox reaction**

Equation 19.4.10: $\Delta G° = -RT \ln K$

**Relationship between Δ *E* ° and *K* for a redox reaction at 25°C**

Equation 19.4.12: $E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ K$

Equation 19.4.13: $E^o_{cell} = \left(\frac{0.0591}{n}\right) log\ K$

**Relationship between Δ *G* ° and *Q***

Equation 19.4.14: $\Delta G = \Delta G° + RT \ln Q$

**Relationship between $E_{cell}$ and $Q$ at 25°C**

Equation 19.4.17: $E_{cell} = E^{o}_{cell} - \frac{0.0591\ V}{F}\ ln\ Q$

## Conceptual Problems

1. State whether you agree or disagree with this reasoning and explain your answer: Standard electrode potentials arise from the number of electrons transferred. The greater the number of electrons transferred, the greater the measured potential difference. If 1 mol of a substance produces 0.76 V when 2 mol of electrons are transferred—as in Zn(s) → $Zn^{2+}$(aq) + $2e^{-}$—then 0.5 mol of the substance will produce 0.76/2 V because only 1 mol of electrons is transferred.
2. What is the relationship between the *measured cell potential* and the *total charge* that passes through a cell? Which of these is dependent on concentration? Which is dependent on the identity of the oxidant or the reductant? Which is dependent on the number of electrons transferred?
3. In the equation $w_{max} = -nFE°_{cell}$, which quantities are extensive properties and which are intensive properties?
4. For any spontaneous redox reaction, $E$ is positive. Use thermodynamic arguments to explain why this is true.
5. State whether you agree or disagree with this statement and explain your answer: Electrochemical methods are especially useful in determining the reversibility or irreversibility of reactions that take place in a cell.
6. Although the sum of two half-reactions gives another half-reaction, the sum of the potentials of the two half-reactions cannot be used to obtain the potential of the net half-reaction. Why? When does the sum of two half-reactions correspond to the overall reaction? Why?
7. Occasionally, you will find high-quality electronic equipment that has its electronic components plated in gold. What is the advantage of this?
8. Blood analyzers, which measure pH, $P(CO_2)$ and $P(O_2)$ are frequently used in clinical emergencies. For example, blood $P(CO_2)$ is measured with a pH electrode covered with a plastic membrane that is permeable to $CO_2$. Based on your knowledge of how electrodes function, explain how such an electrode might work. Hint: $CO_2(g) + H_2O(l) \rightarrow HCO_3^{-}(aq) + H^{+}(aq)$.
9. Concentration cells contain the same species in solution in two different compartments. Explain what produces a voltage in a concentration cell. When does V = 0 in such a cell?
10. Describe how an electrochemical cell can be used to measure the solubility of a sparingly soluble salt.

## Answers

1.
2.
3. extensive: $w_{max}$ and $n$; intensive: $E°_{cell}$
4.
5.
6.
7. Gold is highly resistant to corrosion because of its very positive reduction potential.
8.
9.
10.

## Numerical Problems

1. The chemical equation for the combustion of butane is as follows:

$$C_4H10\,(g) + \frac{13}{2}O_2\,(g) \rightarrow 2CO_2\,(g) + 5H_2O\,(g)$$

This reaction has $\Delta H° = -2877$ kJ/mol. Calculate $E°_{cell}$ and then determine $\Delta G°$. Is this a spontaneous process? What is the change in entropy that accompanies this process at 298 K?

2. How many electrons are transferred during the reaction $Pb(s) + Hg_2Cl_2(s) \rightarrow PbCl_2(aq) + 2Hg(l)$? What is the standard cell potential? Is the oxidation of Pb by $Hg_2Cl_2$ spontaneous? Calculate $\Delta G°$ for this reaction.
3. For the cell represented as $Al(s)\,|\,Al^{3+}(aq)\,\|\,Sn^{2+}(aq),\ Sn^{4+}(aq)\,|\,Pt(s)$, how many electrons are transferred in the redox reaction? What is the standard cell potential? Is this a spontaneous process? What is $\Delta G°$?
4. Explain why the sum of the potentials for the half-reactions $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ and $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ does not equal the potential for the reaction $Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$. What is the net cell potential? Compare the values of $\Delta G°$ for the sum of the potentials and the actual net cell potential.
5. Based on Table 19.3.1 and Table P1, do you agree with the proposed potentials for the following half-reactions? Why or why not?
    1. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, $E° = 0.68$ V
    2. $Ce^{4+}(aq) + 4e^- \rightarrow Ce(s)$, $E° = -0.62$ V
6. For each reaction, calculate $E°_{cell}$ and then determine $\Delta G°$. Indicate whether each reaction is spontaneous.
    1. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
    2. $K_2S_2O_6(aq) + I_2(s) \rightarrow 2KI(aq) + 2K_2SO_4(aq)$
    3. $Sn(s) + CuSO_4(aq) \rightarrow Cu(s) + SnSO_4(aq)$
7. What is the standard change in free energy for the reaction between $Ca^{2+}$ and Na(s) to give Ca(s) and $Na^+$? Do the sign and magnitude of $\Delta G°$ agree with what you would expect based on the positions of these elements in the periodic table? Why or why not?
8. In acidic solution, permanganate ($MnO_4^-$) oxidizes $Cl^-$ to chlorine gas, and $MnO_4^-$ is reduced to $Mn^{2+}(aq)$.
    1. Write the balanced chemical equation for this reaction.
    2. Determine $E°_{cell}$.
    3. Calculate the equilibrium constant.
9. Potentiometric titrations are an efficient method for determining the endpoint of a redox titration. In such a titration, the potential of the solution is monitored as measured volumes of an oxidant or a reductant are added. Data for a typical titration, the potentiometric titration of Fe(II) with a 0.1 M solution of Ce(IV), are given in the following table. The starting potential has been arbitrarily set equal to zero because it is the *change* in potential with the addition of the oxidant that is important.

| Titrant (mL) | $E$ (mV) |
|---|---|
| 2.00 | 50 |
| 6.00 | 100 |
| 9.00 | 255 |
| 10.00 | 960 |
| 11.00 | 1325 |
| 12.00 | 1625 |
| 14.00 | 1875 |

    1. Write the balanced chemical equation for the oxidation of $Fe^{2+}$ by $Ce^{4+}$.
    2. Plot the data and then locate the endpoint.
    3. How many millimoles of $Fe^{2+}$ did the solution being titrated originally contain?
10. The standard electrode potential ($E°$) for the half-reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ is $-0.257$ V. What pH is needed for this reaction to take place in the presence of 1.00 atm $H_2(g)$ as the reductant if $[Ni^{2+}]$ is 1.00 M?

11. The reduction of Mn(VII) to Mn(s) by $H_2(g)$ proceeds in five steps that can be readily followed by changes in the color of the solution. Here is the redox chemistry:

    1. $MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$; $E° = +0.56$ V (purple → dark green)
    2. $MnO_4^{2-}(aq) + 2e^- + 4H^+(aq) \rightarrow MnO_2(s)$; $E° = +2.26$ V (dark green → dark brown solid)
    3. $MnO_2(s) + e^- + 4H^+(aq) \rightarrow Mn^{3+}(aq)$; $E° = +0.95$ V (dark brown solid → red-violet)
    4. $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V (red-violet → pale pink)
    5. $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$; $E° = -1.18$ V (pale pink → colorless)

    1. Is the reduction of $MnO_4^-$ to $Mn^{3+}(aq)$ by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?
    2. Is the reduction of $Mn^{3+}(aq)$ to Mn(s) by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?

12. Mn(III) can disproportionate (both oxidize and reduce itself) by means of the following half-reactions:

    $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V

    $Mn^{3+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + e^-$; $E° = +0.95$ V

    1. What is $E°$ for the disproportionation reaction?
    2. Is disproportionation more or less thermodynamically favored at low pH than at pH 7.0? Explain your answer.
    3. How could you prevent the disproportionation reaction from occurring?

13. For the reduction of oxygen to water, $E° = 1.23$ V. What is the potential for this half-reaction at pH 7.00? What is the potential in a 0.85 M solution of NaOH?

14. The biological molecule abbreviated as NADH (reduced nicotinamide adenine dinucleotide) can be formed by reduction of $NAD^+$ (nicotinamide adenine dinucleotide) via the half-reaction $NAD^+ + H^+ + 2e^- \rightarrow NADH$; $E° = -0.32$ V.

    1. Would NADH be able to reduce acetate to pyruvate?
    2. Would NADH be able to reduce pyruvate to lactate?
    3. What potential is needed to convert acetate to lactate?

    acetate + $CO_2 + 2H^+ + 2e^-$ → pyruvate + $H_2O$; $E° = +0.70$ V

    pyruvare + $2H^+ + 2e^-$ → lactate; $E° = -0.185$ V

15. Given the following biologically relevant half-reactions, will FAD (flavin adenine dinucleotide), a molecule used to transfer electrons whose reduced form is $FADH_2$, be an effective oxidant for the conversion of acetaldehyde to acetate at pH 4.00?

    acetate + $2H^+ + 2e^-$ → acetaldehyde + $H_2O$; $E° = -0.58$ V

    FAD + $2H^+ + 2e^-$ → $FADH_2$; $E° = -0.18$ V

16. Ideally, any half-reaction with $E° > 1.23$ V will oxidize water as a result of the half-reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    1. Will $FeO_4^{2-}$ oxidize water if the half-reaction for the reduction of Fe(VI) → Fe(III) is $FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightarrow Fe^{3+}(aq) + 4H_2O$; $E° = 1.9$ V?
    2. What is the highest pH at which this reaction will proceed spontaneously if $[Fe^{3+}] = [FeO_4^{2-}] = 1.0$ M and <math display="inline" xml:id="av_1.0-19_m077"><semantics><mrow><msub><mi>P</mi><mrow><msub><mtext>O</mtext><mn>2</mn></msub></mrow></msub></mrow></semantics></math> = 1.0 atm?

17. Under acidic conditions, ideally any half-reaction with $E° > 1.23$ V will oxidize water via the reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    1. Will aqueous acidic $KMnO_4$ evolve oxygen with the formation of $MnO_2$?
    2. At pH 14.00, what is $E°$ for the oxidation of water by aqueous $KMnO_4$ (1 M) with the formation of $MnO_2$?
    3. At pH 14.00, will water be oxidized if you are trying to form $MnO_2$ from $MnO_4^{2-}$ via the reactio $2MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_2(s) + O_2(g) + 4OH^-(aq)$?

18. Complexing agents can bind to metals and result in the net stabilization of the complexed species. What is the net thermodynamic stabilization energy that results from using $CN^-$ as a complexing agent for $Mn^{3+}/Mn^{2+}$?

    $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V

$Mn(CN)_6^{3-}(aq) + e^- \rightarrow Mn(CN)_6^{4-}(aq)$; $E° = -0.24V$

19. You have constructed a cell with zinc and lead amalgam electrodes described by the cell diagram Zn(Hg)(s)|$Zn(NO_3)_2$(aq)‖$Pb(NO_3)_2$(aq)|Pb(Hg)(s). If you vary the concentration of $Zn(NO_3)_2$ and measure the potential at different concentrations, you obtain the following data:

| $Zn(NO_3)_2$ (M) | $E_{cell}$ (V) |
|---|---|
| 0.0005 | 0.7398 |
| 0.002 | 0.7221 |
| 0.01 | 0.7014 |

    1. Write the half-reactions that occur in this cell.
    2. What is the overall redox reaction?
    3. What is $E°_{cell}$? What is $\Delta G°$ for the overall reaction?
    4. What is the equilibrium constant for this redox reaction?

20. Hydrogen gas reduces $Ni^{2+}$ according to the following reaction: $Ni^{2+}(aq) + H_2(g) \rightarrow Ni(s) + 2H^+(aq)$; $E°_{cell} = -0.25$ V; $\Delta H = 54$ kJ/mol.

    1. What is $K$ for this redox reaction?
    2. Is this reaction likely to occur?
    3. What conditions can be changed to increase the likelihood that the reaction will occur as written?
    4. Is the reaction more likely to occur at higher or lower pH?

21. The silver–silver bromide electrode has a standard potential of 0.07133 V. What is $K_{sp}$ of AgBr?

## Answers

1.
2.
3. $6e^-$; $E°_{cell} = 1.813$ V; the reaction is spontaneous; $\Delta G° = -525$ kJ/mol Al.
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.
15. yes; $E° = 0.40$ V
16.
17. 1. yes; $E° = 0.45$ V
    2. 0.194 V
    3. yes; $E° = 0.20$ V
18.
19.
20.
21.

## Contributors

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# 19.6: Commercial Galvanic Cells

**Learning Objectives**

- To learn how commercial galvanic cells work.

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A battery (storage cell)A galvanic cell (or series of galvanic cells) that contains all the reactants needed to produce electricity. is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a fuel cellA galvanic cell that requires a constant external supply of one or more reactants to generate electricity. is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

## Batteries

There are two basic kinds of batteries: *disposable*, or *primary*, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and *rechargeable*, or *secondary*, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 19.4.3). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

## Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the Leclanché dry cellA battery consisting of an electrolyte that is an acidic water-based paste containing $MnO_2$, $NH_4Cl$, $ZnCl_2$, graphite, and starch. is actually a “wet cell”: the electrolyte is an acidic water-based paste containing $MnO_2$, $NH_4Cl$, $ZnCl_2$, graphite, and starch (part (a) in Figure 19.5.1). The half-reactions at the anode and the cathode can be summarized as follows:

$$cathode:\ 2MnO_2\,(s) + 2NH_4^+\,(aq) + 2e^- \rightarrow Mn_2O_3\,(s) + 2NH_3\,(aq) + H_2O\,(l)$$

$$anode:\ Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^-$$

The $Zn^{2+}$ ions formed by the oxidation of Zn(s) at the anode react with $NH_3$ formed at the cathode and $Cl^-$ ions present in solution, so the overall cell reaction is as follows:

$$overall:\ 2MnO_2\,(s) + 2NH_4Cl\,(aq) + Zn\,(s) \rightarrow Mn_2O_3\,(s) + Zn\,(NH_3)_2\,Cl_2\,(s) + H_2O\,(l)$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the $MnO_2$ that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with $NH_4Cl$ in the electrolyte, causing the case to corrode and allowing the contents to leak out.

The alkaline batteryA battery that consists of a Leclanché cell adapted to operate under alkaline (basic) conditions. is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

$$cathode:\ 2MnO_2\,(s) + H_2O\,(l) + 2e^- \rightarrow Mn_2O_3\,(s) + 2OH^-\,(aq)$$

$$anode:\ Zn\,(s) + 2OH^-\,(aq) \rightarrow ZnO\,(S) + H_2O\,(l) + 2e^-$$

$$overall:\ 2MnO_2\,(s) + Zn\,(s) \rightarrow Mn_2O_3\,(s) + ZnO\,(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

## Button Batteries

Although some of the small *button* batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or $Ag_2O$ as the oxidant rather than $MnO_2$ (part (b) in Figure 19.13). The cathode and overall reactions and cell output for these two types of button batteries are as follows:

$$cathode\,(Hg):\ HgO\,(s) + H_2O\,(l) + 2e^- \rightarrow Hg\,(l) + 2OH^-\,(aq)$$

$$overall\,(Hg):\ HgO\,(s) + Zn\,(s) \rightarrow Hg\,(l) + ZnO\,(s) \quad E_{cell} = 1.35\ V$$

$$cathode\,(Ag):\ Ag_2O\,(s) + H_2O\,(l) + 2e^- \rightarrow 2Ag\,(s) + 2OH^-\,(aq)$$

$$overall\,(Ag):\ Ag_2O\,(s) + Zn\,(s) \rightarrow 2Ag\,(s) + ZnO\,(s) \quad E_{cell} = 1.6\ V$$

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

## Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries.

One of the few commercially successful water-free batteries is the lithium–iodine batteryA battery that consists of an anode of lithium metal and a cathode containing a solid complex of $I_2$, with a layer of solid LiI in between that allows the diffusion of $Li^+$ ions. The anode is lithium metal, and the cathode is a solid complex of $I_2$. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of $Li^+$ ions. The electrode reactions are as follows:

$$cathode:\ I_2\,(s) + 2e^- \rightarrow 2I^-\,(LiI)$$

$$anode:\ 2Li\,(s) \rightarrow 2Li^+\,(LiI) + 2e^-$$

$$overall:\ 2Li\,(s) + I_2\,(s) \rightarrow 2LiI\,(s) \quad E_{cell} = 3.5\ V$$



**Cardiac pacemaker.** An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure 19.5.1, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using $TiS_2$, for example, for the cathode.

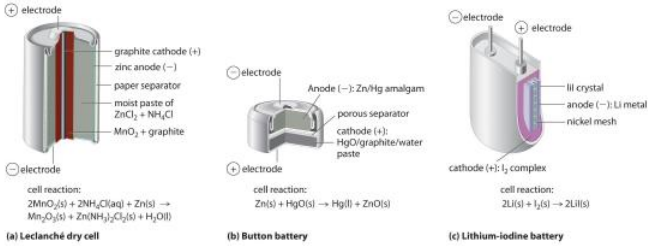



Figure 19.5.1 Three Kinds of Primary (Nonrechargeable) Batteries (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing $MnO_2$, $NH_4Cl$, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or $Ag_2O$ as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of $I_2$. The electrolyte is a layer of solid LiI that allows $Li^+$ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

## Nickel–Cadmium (NiCad) Battery

The nickel–cadmiumA type of battery that consists of a water-based cell with a cadmium anode and a highly oxidized nickel cathode., or *NiCad*, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure 19.5.2, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.




Figure 19.5.2 The Nickel–Cadmium (NiCad) Battery, a Rechargeable **Battery** NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a NiCad battery are as follows:

$$cathode:\ 2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$$

$$anode:\ Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$$

$$overall:\ Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s) \quad E_{cell} = 1.4\ V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they

do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

$$NiO\,(OH)\,(s) + MH \rightarrow Ni\,(OH)_2\,(s) + M\,(s)$$

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

## Lead–Acid (Lead Storage) Battery

The lead–acid batteryA battery consisting of a plate or grid of spongy lead metal, a cathode containing powdered $PbO_2$, and an electrolyte that is usually an aqueous solution of $H_2SO_4$ is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells. As shown in Figure 19.5.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide ($PbO_2$). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M $H_2SO_4$). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

$$cathode:\ 2PbO_2\,(s) + HSO_4^-\,(aq) + 3H^+\,(aq) + 2e^- \rightarrow PbSO_4\,(s) + 2H_2O\,(l) \quad E_{cathode} = 1.685\ V$$

$$anode:\ PbS\,(s) + HSO_4^-\,(aq) \rightarrow PbSO_4\,(s) + H^+\,(aq) + 2e^- \quad E_{anode} = -0.356\ V$$

$$overall:\ 2PbO_2\,(s) + 2HSO_4^-\,(aq) + 2H^+\,(aq) \rightarrow 2bSO_4\,(s) + 2H_2O\,(l) \quad E_{cell} = 2.041\ V$$

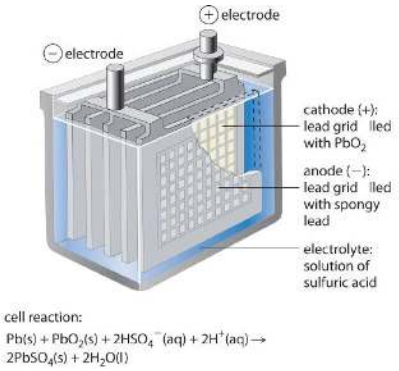



Figure 19.5.3 One Cell of a Lead–Acid Battery The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide ($PbO_2$). The electrolyte is an aqueous solution of sulfuric acid. The value of $E°$ for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte.



Source: Photo courtesy of Mitchclanky2008, http://www.flickr.com/photos/25597837@N05/2422765479/.

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and $PbO_2$. If the battery is recharged too vigorously, however, electrolysis of water can occur, resulting in the evolution of potentially explosive hydrogen gas. (For more information on electrolysis, see Section 19.7.) The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or $PbO_2$ particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

## Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure 19.5.4 . The electrode reactions are as follows:

$$cathode: \ O_2\,(g) + 4H^+ + 4e^- \rightarrow 2H_2O\,(g)$$

$$anode: \ 2H_2\,(g) \rightarrow 4H^+ + 4e^-$$

$$overall: \ 2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$$

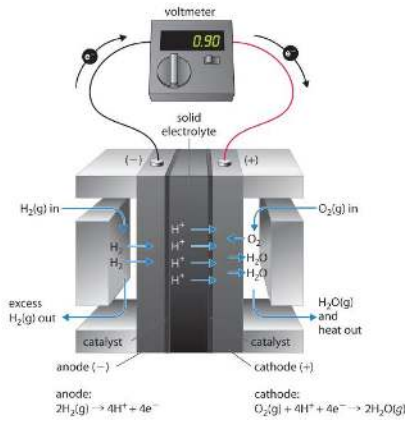



Figure 19.5.4 A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with $H^+$ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2$.

## Summary

A **battery** is a contained unit that produces electricity, whereas a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the **Leclanché dry cell**, which contains an electrolyte in an acidic water-based paste. This battery is called an **alkaline battery** when adapted to operate under alkaline conditions. Button

batteries have a high output-to-mass ratio; **lithium–iodine batteries** consist of a solid electrolyte; the **nickel–cadmium** (NiCad) battery is rechargeable; and the **lead–acid battery**, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

## Key Takeaway

- Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass.

## Conceptual Problems

1. What advantage is there to using an alkaline battery rather than a Leclanché dry cell?
2. Why does the density of the fluid in lead–acid batteries drop when the battery is discharged?
3. What type of battery would you use for each application and why?
    1. powering an electric motor scooter
    2. a backup battery for a smartphone
    3. powering an iPod
4. Why are galvanic cells used as batteries and fuel cells? What is the difference between a battery and a fuel cell? What is the advantage to using highly concentrated or solid reactants in a battery?

## Answer

1. 
2. 
3. 
    1. lead storage battery
    2. lithium–iodine battery
    3. NiCad, NiMH, or lithium ion battery (rechargeable)
4. 

## Numerical Problem

1. This reaction is characteristic of a lead storage battery:

    $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

    If you have a battery with an electrolyte that has a density of 1.15 g/cm$^3$ and contains 30.0% sulfuric acid by mass, is the potential greater than or less than that of the standard cell?

## Answer

1. $[H_2SO_4] = 3.52$ M; $E > E°$

## Contributors

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Modified by Joshua B. Halpern

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# 19.7: Corrosion

**Learning Objectives**

- To understand the process of corrosion.

CorrosionA galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a *patina*. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

## Note the Pattern

Corrosion is a galvanic process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3{\cdot}xH_2O$), commonly known as *rust*, that does not provide a tight protective film (Figure 19.17). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

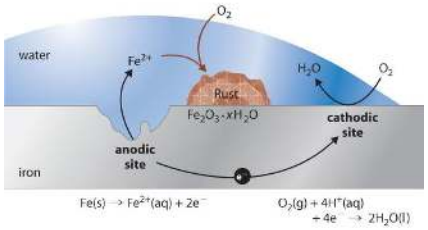



Figure 19.6.1 Rust, the Result of Corrosion of Metallic **Iron**Iron is oxidized to $Fe^{2+}$(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the $Fe^{2+}$ that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3{\cdot}xH_2O$) is formed by the subsequent oxidation of $Fe^{2+}$ by atmospheric oxygen.

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to $Fe^{2+}$; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

$$cathode:\ O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(l) \quad E^o = 1.23\ V$$

$$anode:\ Fe\,(s) \rightarrow Fe^{2+}\,(aq) + 2e^- \quad E^o = -0.24\ V$$

$$overall:\ 2Fe\,(s) + O_2\,(g) + 4H^+\,(aq) \rightarrow 2Fe^{2+}\,(aq) + 2H_2O\,(l) \quad E^o = 1.68\ V$$

The $Fe^{2+}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $Fe^{3+}$, as represented in the following equation:

$$4Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4x)\,H_2O\,(l) \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+$$

The sign and magnitude of $E°$ for the corrosion process (Equation 19.6.3) indicate that there is a strong driving force for the oxidation of iron by $O_2$ under standard conditions (1 M $H^+$). Under neutral conditions, the driving force is somewhat less but still appreciable ($E$ = 1.25 V at pH 7.0). Normally, the reaction of atmospheric $CO_2$ with water to form $H^+$ and $HCO_3^-$ provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 19.6.2).

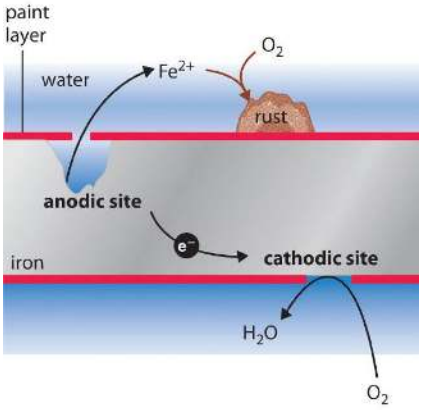



Figure 19.6.2 Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of **Iron** Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to $Fe^{2+}$(aq) at the less exposed site (the anode). Rust is formed when $Fe^{2+}$(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form *under* a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process that will be discussed in Section 19.7. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rat that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 19.6.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

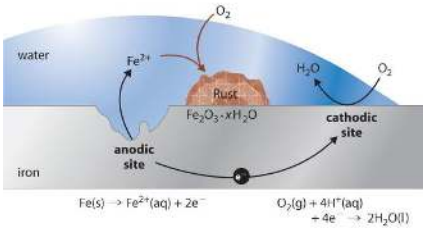



Figure 19.6.3 Galvanic **Corrosion** If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called *cathodic protection*, a more reactive metal such as Zn ($E°$ = −0.76 V for $Zn^{2+} + 2e^- \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$cathode: \ O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

$$anode: \ Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^o = -0.24\ V$$

$$overall: \ 2Zn(s) + O_2(g) + 4H^+(aq) \rightarrow 2Zn^{2+}(aq) + 2H_2O(l)$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying *galvanized steel*, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans. In a similar strategy, sacrificial electrodesAn electrode containing a more reactive metal that is attached to a metal object to inhibit that object’s corrosion. using magnesium, for example, are used to protect underground tanks or pipes (Figure 19.20). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

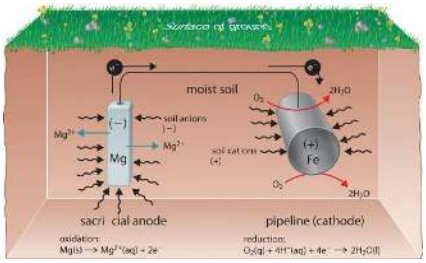



Figure 19.6.4 The Use of a Sacrificial Electrode to Protect Against Corrosion Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E°$ = −2.37 V) is much more easily oxidized than iron ($E°$ = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to $Mg^{2+}$ at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as $H^+$ or $NH_4^+$, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

## Example 19.6.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

1. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°_{cell}$?
2. How could you prevent this corrosion from occurring?

**Given:** identity of metals

**Asked for:** corrosion reaction, $E°_{cell}$, and preventive measures

**Strategy:**

**A** Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°_{cell}$.

**B** Based on the relative redox activity of various substances, suggest possible preventive measures.

**Solution:**

1. **A** According to Table 19.3.1, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E°$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which $O_2$ is reduced, and the iron screws will act as anodes at which iron dissolves:

$$cathode: \ O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^o_{cathode} = 1.23\ V$$

$$anode: \ Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E^o_{anode} = -0.45\ V$$

$$overall: \ 2Fe\,(s) + O_2\,(g) + 4H^+\,(aq) \rightarrow 2Fe^{2+}\,(aq) + 2H_2O\,(l) \quad E^o_{cell} = 1.68\ V$$

Over time, the iron screws will dissolve, and the boat will fall apart.

2. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 19.102).

Exercise

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

1. Do you accept his proposal?
2. What else should you have the plumber do while at your home?

**Answer**

1. Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.
2. Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of $O_2$, promoting oxidation of the more active Fe nearby.

## Summary

The deterioration of metals through oxidation is a galvanic process called **corrosion**. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. **Sacrificial electrodes** can also be attached to an object to protect it.

## Key Takeaway

- Corrosion is a galvanic process that can be prevented using cathodic protection.

## Conceptual Problems

1. Do you expect a bent nail to corrode more or less rapidly than a straight nail? Why?
2. What does it mean when a metal is described as being coated with a sacrificial layer? Is this different from galvanic protection?
3. Why is it important for automobile manufacturers to apply paint to the metal surface of a car? Why is this process particularly important for vehicles in northern climates, where salt is used on icy roads?

## Answer

1.
2.
3. Paint keeps oxygen and water from coming into direct contact with the metal, which prevents corrosion. Paint is more necessary because salt is an electrolyte that increases the conductivity of water and facilitates the flow of electric current between anodic and cathodic sites.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 19.8: Electrolysis

**Learning Objectives**

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called electrolysisAn electrochemical process in which an external voltage is applied to an electrolytic cell to drive a nonspontaneous reaction., occurs: an external voltage is applied to drive a nonspontaneous reaction (Figure 19.1.1). In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

## Note the Pattern

In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M $Cu^{2+}$ solution and the other electrode is cadmium metal immersed in a 1 M $Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to $Cd^{2+}$) and is the anode, while metallic copper will be deposited on the copper electrode ($Cu^{2+}$ is reduced to Cu), which is the cathode (part (a) in Figure 19.7.19). The overall reaction is as follows:

$$Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cu\,(s) + Cd^{2+}\,(aq)$$

This reaction is thermodynamically spntaneous as written (

$$\Delta G^o = nFE^o_{cell} = \left(2\ \cancel{mol\ e^-}\right)\left[96,486\ J/\left(\cancel{V}\cdot\cancel{mol}\right)\right]\left(0.74\ \cancel{V}\right) = -140\ kJ/mol$$

In this direction, the system is acting as a galvanic cell.

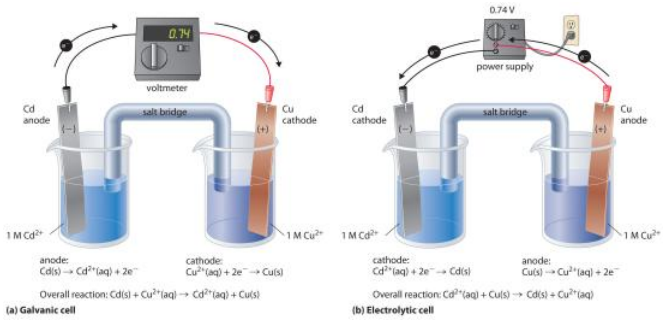



Figure 19.7.1 An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell (a) When compartments that contain a Cd electrode immersed in 1 M $Cd^{2+}$(aq) and a Cu electrode immersed in 1 M $Cu^{2+}$(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to $Cd^{2+}$(aq) at the anode, and $Cu^{2+}$(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to $Cu^{2+}$(aq)] and into the Cd electrode [which is now the cathode, at which $Cd^{2+}$(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is *positive* because electrons are flowing from it, whereas the cathode is *negative* because electrons are flowing into it.

The reverse reaction, the reduction of $Cd^{2+}$ by Cu, is thermodynamically nonspontaneous and will occur only with an *input* of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode ($Cd^{2+}$ is reduced) (part (b) in Figure 19.21). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

$$cathode:\ Cd^{2+}\,(aq) + 2e^- \rightarrow Cd\,(s) \quad E^o_{cathode} = -0.40\ V$$

$$anode:\ Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2e^- \quad E^o_{anode} = 0.34\ V$$

$$overall:\ Cd^{2+}\,(aq) + Cu\,(s) \rightarrow Cu^{2+}\,(aq) + Cd\,(s) \quad E^o_{cell} = -0.74\ V$$

Because $E°_{cell} < 0$, the overall reaction—the reduction of $Cd^{2+}$ by Cu—clearly cannot occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 19.7.1.

**Table 19.7.1 Comparison of Galvanic and Electrolytic Cells**

| Property | Galvanic Cell | Electrolytic Cell |
|---|---|---|
| $\Delta G$ | < 0 | > 0 |
| $E_{cell}$ | > 0 | < 0 |
| **Electrode Process** | | |
| anode | oxidation | oxidation |
| cathode | reduction | reduction |
| **Sign of Electrode** | | |
| anode | − | + |
| cathode | + | − |

## Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, $Cl^-$ is oxidized at the anode, and $Na^+$ is reduced at the cathode. The overall reaction is as follows:

$$2NaCl\,(l) \rightarrow Na\,(l) + Cl_2\,(g)$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is *liquid* sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a *Downs cell* (Figure 19.7.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

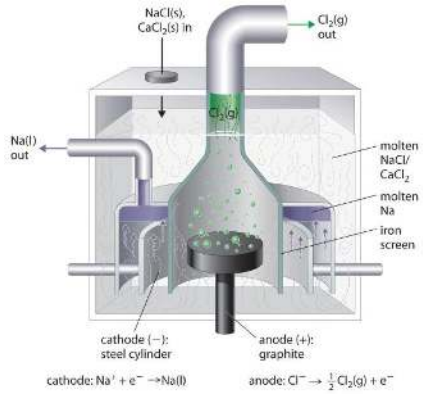



Figure 19.7.2 A Downs Cell for the Electrolysis of Molten NaCl The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.

Similarly, in the *Hall–Heroult process* used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide ($Al_2O_3$; melting point = 2054°C) and 95% cryolite ($Na_3AlF_6$; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and $CO_2$ gas at the carbon anode. The overall reaction is as follows:

$$2Al_2O_3\,(l) + 3C\,(s) \rightarrow 4Al\,(l) + 3CO_2\,(g)$$

Oxide ions react with oxidized carbon at the anode, producing $CO_2(g)$.

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table 19.3.1 and Table P1, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, $Cl^-$ is oxidized because it is the only anion present, but either $Na^+$ or $Ca^{2+}$ can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced ($Al^{3+}$), but there are three species that can be oxidized: C, $O^{2-}$, and $F^-$.

In the Hall–Heroult process, C is oxidized instead of $O^{2-}$ or $F^-$ because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either $O_2$ or $F_2$. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca ($\chi$ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, $Na^+$ more difficult to reduce. In fact, the reduction of $Na^+$ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

### Example 19.7.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

**Given:** identity of salts

**Asked for:** electrolysis products

**Strategy:**

**A** List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 3.3.9, determine which species will be reduced and which species will be oxidized.

**B** Identify the products that will form at each electrode.

**Solution:**

**A** The possible reduction products are Mg and K, and the possible oxidation products are $Cl_2$ and $Br_2$. Because Mg is more electronegative than K ($\chi$ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), $Cl_2$ is a stronger oxidant than $Br_2$.

**B** Electrolysis will therefore produce $Br_2$ at the anode and Mg at the cathode.

Exercise

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

**Answer:** $Br_2$ and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: $H_2$ and $O_2$. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as $H_2SO_4$ or $Na_2SO_4$) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of $H_2$ and $O_2$ (Figure 19.7.3). The reactions that occur are as follows:

$$cathode:\ 2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^o_{cathode} = 0\ V$$

$$anode:\ 2H_2O(l) \rightarrow O_2(g) + 4H^+(g) + 4e^- \quad E^o_{anode} = 1.23\ V$$

$$overall:\ 2H_2O(l) \rightarrow O_2(g) + 2H_2(g) \quad E^o_{cell} = -1.23\ V$$

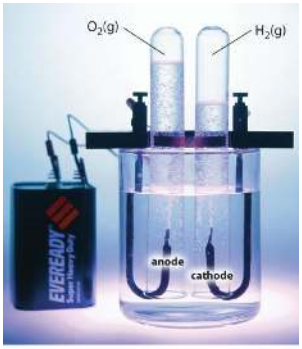



Figure 19.7.3 The Electrolysis of Water Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as $H_2SO_4$ or $Na_2SO_4$ drives the thermodynamically nonspontaneous decomposition of water into $H_2$ at the cathode and $O_2$ at the anode.

For a system that contains an electrolyte such as $Na_2SO_4$, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P(O_2) = P(H_2) = 1$ atm, we can use the standard potentials and Equation 19.4.17 to calculate $E$ for the overall reaction:

$$E_{cell} = E^o_{cell} - \left(\frac{0.0591\ V}{n}\right) log\ \left(P_{O_2} P^2_{H_2}\right)$$

$$E_{cell} = -1.23\ V - \left(\frac{0.0591\ V}{4}\right) log\ (1) = -1.23\ V$$

Thus $E_{cell}$ is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M $H^+$ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an overvoltageThe voltage that must be applied in electrolysis in addition to the calculated (theoretical) value to overcome factors such as a high activation energy and the formation of bubbles on a surface., represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does *not* react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The *p*-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to $O_2$ can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only $F_2$ cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as $NO_3^-$, $SO_4^{2-}$, $PO_4^{3-}$, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

### Note the Pattern

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.

## Electroplating

In a process called electroplatingA process in which a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis., a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 19.7.4.

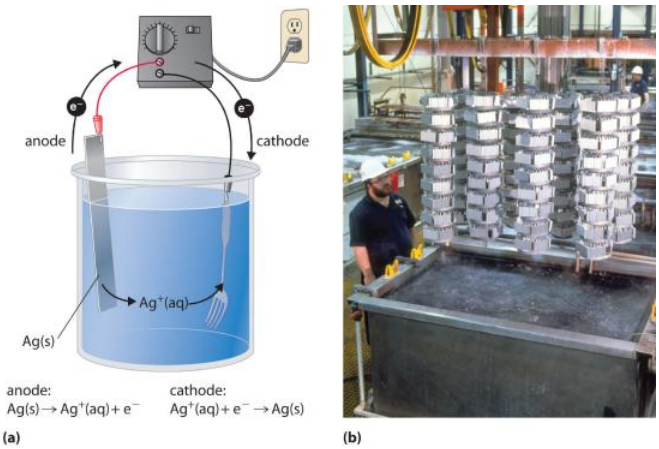



Figure 19.7.4 Electroplating (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the $Ag^+$ solution and applying the correct potential.

The half-reactions in electroplating a fork, for example, with silver are as follows:

$$cathode\,(fork):\ \ Ag^+\,(aq) + e^- \rightarrow Ag\,(s) \quad E^o_{cathode} = 0.80\ V$$

$$anode\,(silverbar):\ \ Ag\,(s) \rightarrow Ag^+\,(aq) + e^- \quad E^o_{anode} = 0.80\ V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell}$ = 0 V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

## Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of $Ag^+$ to Ag metal. In contrast, in the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of $Cu^{2+}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 *F*), which is equal to 96,486 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (C) transferred is the product of the current (A) and the time (*t*, in seconds):

$$C = A \times t$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$charge = (0.60\ A)\left(6.0\ \cancel{min}\right)\left(60\ s/\cancel{min}\right) = 220A \cdot s$$

The number of moles of electrons transferred to $Cu^{2+}$ is therefore

$$moles\ e^- = \frac{220\ \cancel{C}}{96,486\ \cancel{C}/mol} = 2.3 \times 10^{-3}\ mol\ e^-$$

Because two electrons are required to reduce a single $Cu^{2+}$ ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or $1.2 \times 10^{-3}$ mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much

higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 *F*/s, and reaction times are on the order of 3–4 weeks.

### Example 19.7.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

**Given:** mass of metal, time, and efficiency

**Asked for:** current required

**Strategy:**

**A** Calculate the number of moles of metal corresponding to the given mass transferred.

**B** Write the reaction and determine the number of moles of electrons required for the electroplating process.

**C** Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

**Solution:**

**A** We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$moles\ Ag = \frac{2.0\ \cancel{g}}{107.868\ \cancel{g}/mol} = 1.85 \times 10^{-2}\ mol\ Ag$$

**B** The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

**C** Using the definition of the faraday,

$$Coulombs = \left(1.85 \times 10^{-2}\ \cancel{mol}\right)\left(96,486\ C/\cancel{mol}\right) = 1.78 \times 10^{3}\ C$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$amperes = \frac{1.78 \times 10^{3}\ C}{\left(12.0\ \cancel{h}\right)\left(60\ \cancel{min}/\cancel{h}\right)\left(60\ s/\cancel{min}\right)}$$

$$= 4.12 \times 10^{-2}\ C/s = 4.12 \times 10^{-2}\ A$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten $Al_2O_3/Na_3AlF_6$ mixture?

**Answer:** 5.8 h

### Summary

In **electrolysis**, an external voltage is applied to drive a nonspontaneous reaction. A Downs cell is used to produce sodium metal from a mixture of salts, and the Hall–Heroult process is used to produce aluminum commercially. Electrolysis can also be used to produce $H_2$ and $O_2$ from water. In practice, an additional voltage, called an **overvoltage**, must be applied to overcome factors such as a large activation energy and a junction potential. **Electroplating** is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

### Key Takeaways

- In electrolysis, an external voltage is applied to drive a nonspontaneous reaction.
- The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred.

## Key Equation

**Relationship of charge, current and time**

Equation 19.116: $C = A \times t$

## Conceptual Problems

1. Why might an electrochemical reaction that is thermodynamically favored require an overvoltage to occur?
2. How could you use an electrolytic cell to make quantitative comparisons of the strengths of various oxidants and reductants?
3. Why are mixtures of molten salts, rather than a pure salt, generally used during electrolysis?
4. Two solutions, one containing $Fe(NO_3)_2 \cdot 6H_2O$ and the other containing the same molar concentration of $Fe(NO_3)_3 \cdot 6H_2O$, were electrolyzed under identical conditions. Which solution produced the most metal? Justify your answer.

## Numerical Problems

1. The electrolysis of molten salts is frequently used in industry to obtain pure metals. How many grams of metal are deposited from these salts for each mole of electrons?
    1. $AlCl_3$
    2. $MgCl_2$
    3. $FeCl_3$
2. Electrolysis is the most direct way of recovering a metal from its ores. However, the $Na^+(aq)/Na(s)$, $Mg^{2+}(aq)/Mg(s)$, and $Al^{3+}(aq)/Al(s)$ couples all have standard electrode potentials ($E°$) more negative than the reduction potential of water at pH 7.0 (−0.42 V), indicating that these metals can never be obtained by electrolysis of aqueous solutions of their salts. Why? What reaction would occur instead?
3. What volume of chlorine gas at standard temperature and pressure is evolved when a solution of $MgCl_2$ is electrolyzed using a current of 12.4 A for 1.0 h?
4. What mass of copper metal is deposited if a 5.12 A current is passed through a $Cu(NO_3)_2$ solution for 1.5 h.
5. What mass of $PbO_2$ is reduced when a current of 5.0 A is withdrawn over a period of 2.0 h from a lead storage battery?
6. Electrolysis of $Cr^{3+}(aq)$ produces $Cr^{2+}(aq)$. If you had 500 mL of a 0.15 M solution of $Cr^{3+}(aq)$, how long would it take to reduce the $Cr^{3+}$ to $Cr^{2+}$ using a 0.158 A current?
7. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
    1. $AgNO_3$
    2. RbI
8. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
    1. $MgBr_2$
    2. $Hg(CH_3CO_2)_2$
    3. $Al_2(SO_4)_3$

## Answers

1. 
2. 
3. 5.2 L
4. 
5. 
6. 
7. 1. cathode: Ag(s); anode: $O_2(g)$;
    2. cathode: $H_2(g)$; anode: $I_2(s)$

8.

## Contributors

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Modified by Joshua B. Halpern

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# CHAPTER OVERVIEW

## 20: Periodic Trends and the s-Block Elements


20.1: Introduction
20.2: Overview of Periodic Trends
20.3: The Chemistry of Hydrogen
20.4: The Alkali Metals (Group 1)
20.5: The Alkaline Earth Metals (Group 2)
20.6: The s-Block Elements in Biology
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# 20.1: Introduction

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In previous chapters, we used the principles of chemical bonding, thermodynamics, and kinetics to provide a conceptual framework for understanding the chemistry of the elements. Beginning in Chapter 21, we use the periodic table to guide our discussion of the properties and reactions of the elements and the synthesis and uses of some of their commercially important compounds. We begin this chapter with a review of periodic trends as an introduction, and then we describe the chemistry of hydrogen and the other *s*-block elements. In Chapter 22, we consider the chemistry of the *p*-block elements; Chapter 23 presents the transition metals, in which the *d*-subshell is being filled. In this chapter, you will learn why potassium chloride is used as a substitute for sodium chloride in a low-sodium diet, why cesium is used as a photosensor, why the heating elements in electric ranges are coated with magnesium oxide, and why exposure to a radioactive isotope of strontium is more dangerous for children than for adults.

**Flame tests**. Heating a comp flame results in the formation of its component atoms in electronically excited states. When an excited atom decays to the gr light. Each element emits light at characteristic frequencies. Flame tests are used to identify many elements based on the color o he visible region of the electromagnetic spectrum. As shown here, sodium compounds produce an intense yellow light, whereas ıds produce a crimson color.

## Contributors

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# 20.2: Overview of Periodic Trends

**Learning Objectives**

- To know important periodic trends in several atomic properties.

As we begin our summary of periodic trends, recall that the single most important unifying principle in understanding the chemistry of the elements is the systematic increase in atomic number, accompanied by the orderly filling of atomic orbitals by electrons, which leads to periodicity in such properties as atomic and ionic size, ionization energy, electronegativity, and electron affinity. The same factors also lead to periodicity in valence electron configurations, which for each group results in similarities in oxidation states and the formation of compounds with common stoichiometries.

The most important periodic trends in atomic properties are summarized in Figure 20.2.1. Recall that these trends are based on periodic variations in a single fundamental property, the **effective nuclear charge** ($Z_{eff}$), which increases from left to right and from top to bottom in the periodic table.

The diagonal line in Figure 20.2.1 separates the metals (to the left of the line) from the nonmetals (to the right of the line). Because metals have relatively low electronegativities, they tend to lose electrons in chemical reactions to elements that have relatively high electronegativities, forming compounds in which they have positive oxidation states. Conversely, nonmetals have high electronegativities, and they therefore tend to gain electrons in chemical reactions to form compounds in which they have negative oxidation states. The semimetals lie along the diagonal line dividing metals and nonmetals. It is not surprising that they tend to exhibit properties and reactivities intermediate between those of metals and nonmetals. Because the elements of groups 13, 14, and 15 span the diagonal line separating metals and nonmetals, their chemistry is more complex than predicted based solely on their valence electron configurations.

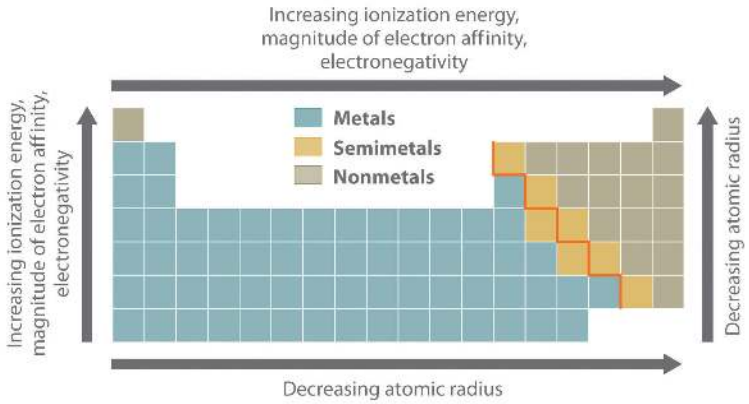



Figure 20.2.1: Summary of Periodic Trends in Atomic Properties. Ionization energies, the magnitude of electron affinities, and electronegativities generally increase from left to right and from bottom to top. In contrast, atomic size decreases from left to right and from bottom to top. Consequently, the elements in the upper right of the periodic table are the smallest and most electronegative; the elements in the bottom left are the largest and least electronegative. The semimetals lie along the diagonal line separating the metals from the nonmetals and exhibit intermediate properties.

## Unique Chemistry of the Lightest Elements

The chemistry of the second-period element of each group (n = 2: Li, Be, B, C, N, O, and F) differs in many important respects from that of the heavier members, or congeners, of the group. Consequently, the elements of the third period (n = 3: Na, Mg, Al, Si, P, S, and Cl) are generally more representative of the group to which they belong. The anomalous chemistry of second-period elements results from three important characteristics: small radii, energetically unavailable d orbitals, and a tendency to form pi (π) bonds with other atoms.

> *In contrast to the chemistry of the second-period elements, the chemistry of the third-period elements is more representative of the chemistry of the respective group.*

Due to their small radii, second-period elements have electron affinities that are less negative than would be predicted from general periodic trends. When an electron is added to such a small atom, increased electron–electron repulsions tend to destabilize the anion. Moreover, the small sizes of these elements prevent them from forming compounds in which they have more than four nearest neighbors. Thus $BF_3$ forms only the four-coordinate, tetrahedral $BF_4^-$ ion, whereas under the same conditions $AlF_3$ forms the six-coordinate, octahedral $AlF_6^{3-}$ ion. Because of the smaller atomic size, simple binary ionic compounds of second-period elements also have more covalent character than the corresponding compounds formed from their heavier congeners. The very small cations derived from second-period elements have a high charge-to-radius ratio and can therefore polarize the filled valence shell of an anion. As such, the bonding in such compounds has a significant covalent component, giving the compounds properties that can differ significantly from those expected for simple ionic compounds. As an example, LiCl, which is partially covalent in character, is much more soluble than NaCl in solvents with a relatively low dielectric constant, such as ethanol ($\varepsilon$ = 25.3 versus 80.1 for $H_2O$).

Because d orbitals are never occupied for principal quantum numbers less than 3, the valence electrons of second-period elements occupy 2s and 2p orbitals only. The energy of the 3d orbitals far exceeds the energy of the 2s and 2p orbitals, so using them in bonding is energetically prohibitive. Consequently, electron configurations with more than four electron pairs around a central, second-period element are simply not observed. You may recall that the role of d orbitals in bonding in main group compounds with coordination numbers of 5 or higher remains somewhat controversial. In fact, theoretical descriptions of the bonding in molecules such as $SF_6$ have been published without mentioning the participation of d orbitals on sulfur. Arguments based on d-orbital availability and on the small size of the central atom, however, predict that coordination numbers greater than 4 are unusual for the elements of the second period, which is in agreement with experimental results.

One of the most dramatic differences between the lightest main group elements and their heavier congeners is the tendency of the second-period elements to form species that contain multiple bonds. For example, N is just above P in group 15: $N_2$ contains an N≡N bond, but each phosphorus atom in tetrahedral $P_4$ forms three P–P bonds. This difference in behavior reflects the fact that within the same group of the periodic table, the relative energies of the π bond and the sigma (σ) bond differ. A C=C bond, for example, is approximately 80% stronger than a C–C bond. In contrast, an Si=Si bond, with less p-orbital overlap between the valence orbitals of the bonded atoms because of the larger atomic size, is only about 40% stronger than an Si–Si bond. Consequently, compounds that contain both multiple and single C to C bonds are common for carbon, but compounds that contain only sigma Si–Si bonds are more energetically favorable for silicon and the other third-period elements.

Another important trend to note in main group chemistry is the chemical similarity between the lightest element of one group and the element immediately below and to the right of it in the next group, a phenomenon known as the diagonal effect (Figure 20.2.2) There are, for example, significant similarities between the chemistry of Li and Mg, Be and Al, and B and Si. Both $BeCl_2$ and $AlCl_3$ have substantial covalent character, so they are somewhat soluble in nonpolar organic solvents. In contrast, although Mg and Be are in the same group, $MgCl_2$ behaves like a typical ionic halide due to the lower electronegativity and larger size of magnesium.

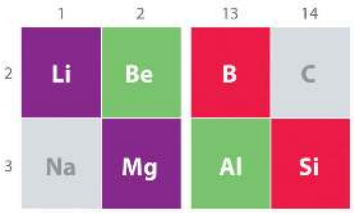



Figure 20.2.2: The Diagonal Effect. The properties of the lightest element in a group are often more similar to those of the element below and to the right in the periodic table. For instance, the chemistry of lithium is more similar to that of magnesium in group 2 than it is to the chemistry of sodium, the next member in group 1.

## The Inert-Pair Effect

The **inert-pair effect** refers to the empirical observation that the heavier elements of groups 13–17 often have oxidation states that are lower by 2 than the maximum predicted for their group. For example, although an oxidation state of +3 is common for group 13 elements, the heaviest element in group 13, thallium (Tl), is more likely to form compounds in which it has a +1 oxidation state. There appear to be two major reasons for the inert-pair effect: increasing ionization energies and decreasing bond strengths.

> *In moving down a group in the p-block, increasing ionization energies and decreasing bond strengths result in an inert-pair effect.*

The ionization energies increase because filled (n − 1)d or (n − 2)f subshells are relatively poor at shielding electrons in ns orbitals. Thus the two electrons in the ns subshell experience an unusually high effective nuclear charge, so they are strongly attracted to the nucleus, reducing their participation in bonding. It is therefore substantially more difficult than expected to remove these $ns^2$electrons, as shown in Table 20.2.1 by the difference between the first ionization energies of thallium and aluminum. Because Tl is less likely than Al to lose its two $ns^2$ electrons, its most common oxidation state is +1 rather than +3.

Table 20.2.1: Ionization Energies (I) and Average M–Cl Bond Energies for the Group 13 Elements

| Element | Electron Configuration | $I_1$ (kJ/mol) | $I_1 + I_2 + I_3$ (kJ/mol) | Average M–Cl Bond Energy (kJ/mol) |
|---|---|---|---|---|
| B | $[He]\ 2s^2 2p^1$ | 801 | 6828 | 536 |
| Al | $[Ne]\ 3s^2 3p^1$ | 578 | 5139 | 494 |
| Ga | $[Ar]\ 3d^{10} 4s^2 4p^1$ | 579 | 5521 | 481 |
| In | $[Kr]\ 4d^{10} 5s^2 p^1$ | 558 | 5083 | 439 |
| Tl | $[Xe]\ 4f^{14} 5d^{10} 6s^2 p^1$ | 589 | 5439 | 373 |

Source of data: John A. Dean, Lange's Handbook of Chemistry, 15th ed. (New York: McGraw-Hill, 1999).

Going down a group, the atoms generally became larger, and the overlap between the valence orbitals of the bonded atoms decreases. Consequently, bond strengths tend to decrease down a column. As shown by the M–Cl bond energies listed in Table 20.2.1, the strength of the bond between a group 13 atom and a chlorine atom decreases by more than 30% from B to Tl. Similar decreases are observed for the atoms of groups 14 and 15.

The net effect of these two factors—increasing ionization energies and decreasing bond strengths—is that in going down a group in the p-block, the additional energy released by forming two additional bonds eventually is not great enough to compensate for the additional energy required to remove the two $ns^2$ electrons.

### ✔ Example 20.2.1

Based on the positions of the group 13 elements in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +1 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of another group will exhibit chemistry most similar to that of Al.

**Given:** positions of elements in the periodic table

**Asked for:** classification, oxidation-state stability, and chemical reactivity

**Strategy:**

From the position of the diagonal line in the periodic table separating metals and nonmetals, classify the group 13 elements. Then use the trends discussed in this section to compare their relative stabilities and chemical reactivities.

**Solution**

a. Group 13 spans the diagonal line separating the metals from the nonmetals. Although Al and B both lie on the diagonal line, only B is a semimetal; the heavier elements are metals.
b. All five elements in group 13 have an $ns^2np^1$ valence electron configuration, so they are expected to form ions with a +3 charge from the loss of all valence electrons. The inert-pair effect should be most important for the heaviest element (Tl), so it is most likely to form compounds in an oxidation state that is lower by 2. Thus the +1 oxidation state is predicted to be

most important for thallium.

c. Among the main group elements, the lightest member of each group exhibits unique chemistry because of its small size resulting in a high concentration of charge, energetically unavailable d orbitals, and a tendency to form multiple bonds. In group 13, we predict that the chemistry of boron will be quite different from that of its heavier congeners.

d. Within the s and p blocks, similarities between elements in different groups are most marked between the lightest member of one group and the element of the next group immediately below and to the right of it. These elements exhibit similar electronegativities and charge-to-radius ratios. Because Al is the second member of group 13, we predict that its chemistry will be most similar to that of Be, the lightest member of group 2.

### ? Exercise 20.2.1

Based on the positions of the group 14 elements C, Si, Ge, Sn, and Pb in the periodic table and the general trends outlined in this section,

a. classify these elements as metals, semimetals, or nonmetals.
b. predict which element forms the most stable compounds in the +2 oxidation state.
c. predict which element differs the most from the others in its chemistry.
d. predict which element of group 14 will be chemically most similar to a group 15 element.

**Answer**

a. nonmetal: C; semimetals: Si and Ge; metals: Sn and Pb
b. Pb is most stable as $M^{2+}$.
c. C is most different.
d. C and P are most similar in chemistry.

## Summary

The chemistry of the third-period element in a group is most representative of the chemistry of the group because the chemistry of the second-period elements is dominated by their small radii, energetically unavailable d orbitals, and tendency to form π bonds with other atoms. The most important unifying principle in describing the chemistry of the elements is that the systematic increase in atomic number and the orderly filling of atomic orbitals lead to periodic trends in atomic properties. The most fundamental property leading to periodic variations is the effective nuclear charge ($Z_{eff}$). Because of the position of the diagonal line separating metals and nonmetals in the periodic table, the chemistry of groups 13, 14, and 15 is relatively complex. The second-period elements (n = 2) in each group exhibit unique chemistry compared with their heavier congeners because of their smaller radii, energetically unavailable d orbitals, and greater ability to form π bonds with other atoms. Increasing ionization energies and decreasing bond strengths lead to the inert-pair effect, which causes the heaviest elements of groups 13–17 to have a stable oxidation state that is lower by 2 than the maximum predicted for their respective groups.

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# 20.3: The Chemistry of Hydrogen

**Learning Objectives**

- To describe the physical and chemical properties of hydrogen and predict its reactivity.

We now turn from an overview of periodic trends to a discussion of the s-block elements, first by focusing on hydrogen, whose chemistry is sufficiently distinct and important to be discussed in a category of its own. Most versions of the periodic table place hydrogen in the upper left corner immediately above lithium, implying that hydrogen, with a $1s^1$ electron configuration, is a member of group 1. In fact, the chemistry of hydrogen does not greatly resemble that of the metals of Group 1. Indeed, some versions of the periodic table place hydrogen above fluorine in Group 17 because the addition of a single electron to a hydrogen atom completes its valence shell.

> *Although hydrogen has an $ns^1$ electron configuration, its chemistry does not resemble that of the Group 1 metals.*

## Isotopes of Hydrogen

Hydrogen, the most abundant element in the universe, is the ultimate source of all other elements by the process of nuclear fusion. Table 20.3.1 "The Isotopes of Hydrogen" compares the three isotopes of hydrogen, all of which contain one proton and one electron per atom. The most common isotope is **protium** ($^1$H or H), followed by **deuterium** ($^2$H or D), which has an additional neutron. The rarest isotope of hydrogen is **tritium** ($^3$H or T), which is produced in the upper atmosphere by a nuclear reaction when cosmic rays strike nitrogen and other atoms; it is then washed into the oceans by rainfall. Tritium is radioactive, decaying to $^3$He with a half-life of only 12.32 years. Consequently, the atmosphere and oceans contain only a very low, steady-state level of tritium. The term hydrogen and the symbol H normally refer to the naturally occurring mixture of the three isotopes.

Table 20.3.1: The Isotopes of Hydrogen

| | Protium | Deuterium | Tritium |
|---|---|---|---|
| symbol | $^1_1$H | $^2_1$H | $^3_1$H |
| neutrons | 0 | 1 | 2 |
| mass (amu) | 1.00783 | 2.0140 | 3.01605 |
| abundance (%) | 99.9885 | 0.0115 | ~$10^{-17}$ |
| half-life (years) | — | — | 12.32 |
| boiling point of $X_2$ (K) | 20.28 | 23.67 | 25 |
| melting point/boiling point of $X_2O$ (°C) | 0.0/100.0 | 3.8/101.4 | 4.5/? |

The different masses of the three isotopes of hydrogen cause them to have different physical properties. Thus $H_2$, $D_2$, and $T_2$ differ in their melting points, boiling points, densities, and heats of fusion and vaporization. In 1931, Harold Urey and coworkers discovered deuterium by slowly evaporating several liters of liquid hydrogen until a volume of about 1 mL remained. When that remaining liquid was vaporized and its emission spectrum examined, they observed new absorption lines in addition to those previously identified as originating from hydrogen. The natural abundance of tritium, in contrast, is so low that it could not be detected by similar experiments; it was first prepared in 1934 by a nuclear reaction.

**Harold Urey (1893–1981)**

Urey won the Nobel Prize in Chemistry in 1934 for his discovery of deuterium ($^2$H). Urey was born and educated in rural Indiana. After earning a BS in zoology from the University of Montana in 1917, Urey changed career directions. He earned his

PhD in chemistry at Berkeley with G. N. Lewis and subsequently worked with Niels Bohr in Copenhagen. During World War II, Urey was the director of war research for the Atom Bomb Project at Columbia University. In later years, his research focused on the evolution of life. In 1953, he and his graduate student, Stanley Miller, showed that organic compounds, including amino acids, could be formed by passing an electric discharge through a mixture of compounds thought to be present in the atmosphere of primitive Earth.

Because the normal boiling point of $D_2O$ is 101.4°C (compared to 100.0°C for $H_2O$), evaporation or fractional distillation can be used to increase the concentration of deuterium in a sample of water by the selective removal of the more volatile $H_2O$. Thus bodies of water that have no outlet, such as the Great Salt Lake and the Dead Sea, which maintain their level solely by evaporation, have significantly higher concentrations of deuterated water than does lake or seawater with at least one outlet. A more efficient way to obtain water highly enriched in deuterium is by prolonged electrolysis of an aqueous solution. Because a deuteron ($D^+$) has twice the mass of a proton ($H^+$), it diffuses more slowly toward the electrode surface. Consequently, the gas evolved at the cathode is enriched in H, the species that diffuses more rapidly, favoring the formation of $H_2$ over $D_2$ or HD. Meanwhile, the solution becomes enriched in deuterium. Deuterium-rich water is called heavy water because the density of $D_2O$ (1.1044 g/cm$^3$ at 25°C) is greater than that of $H_2O$ (0.99978 g/cm$^3$). Heavy water was an important constituent of early nuclear reactors.

Because deuterons diffuse so much more slowly, $D_2O$ will not support life and is actually toxic if administered to mammals in large amounts. The rate-limiting step in many important reactions catalyzed by enzymes involves proton transfer. The transfer of $D^+$ is so slow compared with that of $H^+$ because bonds to D break more slowly than those to H, so the delicate balance of reactions in the cell is disrupted. Nonetheless, deuterium and tritium are important research tools for biochemists. By incorporating these isotopes into specific positions in selected molecules, where they act as labels, or tracers, biochemists can follow the path of a molecule through an organism or a cell. Tracers can also be used to provide information about the mechanism of enzymatic reactions.

## Bonding in Hydrogen and Hydrogen-Containing Compounds

The $1s^1$ electron configuration of hydrogen indicates a single valence electron. Because the 1s orbital has a maximum capacity of two electrons, hydrogen can form compounds with other elements in three ways (Figure 20.3.1):

1. **Losing its electron to form a proton ($H^+$) with an empty 1s orbital.** The proton is a Lewis acid that can accept a pair of electrons from another atom to form an electron-pair bond. In the acid–base reactions, the proton always binds to a lone pair of electrons on an atom in another molecule to form a polar covalent bond. If the lone pair of electrons belongs to an oxygen atom of a water molecule, the result is the hydronium ion ($H_3O^+$).
2. **Accepting an electron to form a hydride ion ($H^-$), which has a filled $1s^2$ orbital.** Hydrogen reacts with relatively electropositive metals, such as the alkali metals (group 1) and alkaline earth metals (group 2), to form ionic hydrides, which contain metal cations and $H^-$ ions.
3. **Sharing its electron with an electron on another atom to form an electron-pair bond.** With a half-filled $1s^1$ orbital, the hydrogen atom can interact with singly occupied orbitals on other atoms to form either a covalent or a polar covalent electron-pair bond, depending on the electronegativity of the other atom.

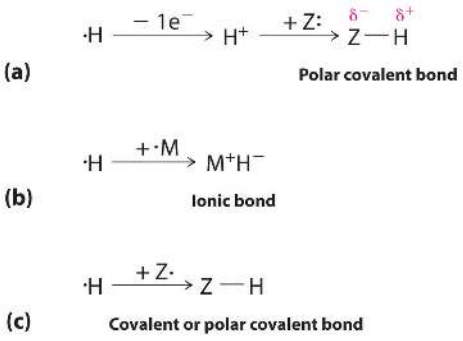



Figure 20.3.1: Three Types of Bonding in Compounds of Hydrogen. Because of its $1s^1$ electron configuration and the fact that the 1s orbital can accommodate no more than two electrons, hydrogen can (a) bond to other elements by losing an electron to form a proton, which can accept a pair of electrons from a more electronegative atom to form a polar covalent bond; (b) gain an electron from an electropositive metal to form a hydride ion, resulting in an ionic hydride; or (c) share its half-filled 1s orbital with a half-filled orbital on another atom to form a covalent or a polar covalent electron-pair bond.

Hydrogen can also act as a bridge between two atoms. One familiar example is the **hydrogen bond**, an electrostatic interaction between a hydrogen bonded to an electronegative atom and an atom that has one or more lone pairs of electrons (Figure 20.3.2). An example of this kind of interaction is the hydrogen bonding network found in water (Figure 20.3.2). Hydrogen can also form a **three-center bond (or electron-deficient bond)**, in which a hydride bridges two electropositive atoms. Compounds that contain hydrogen bonded to boron and similar elements often have this type of bonding. The B–H–B units found in boron hydrides cannot be described in terms of localized electron-pair bonds.

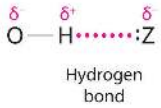



Figure 20.3.2: The Hydrogen Bond. The covalent bond between hydrogen and a very electronegative element, such as nitrogen, oxygen, or fluorine, is highly polar. The resulting partial positive charge on H allows it to interact with a lone pair of electrons on another atom to form a hydrogen bond, which is typically a linear arrangement of the three atoms, with the hydrogen atom placed asymmetrically between the two heavier atoms.

Because the H atom in the middle of such a unit can accommodate a maximum of only two electrons in its 1s orbital, the B–H–B unit can be described as containing a hydride that interacts simultaneously with empty $sp^3$ orbitals on two boron atoms (Figure 20.3.3). In these bonds, only two bonding electrons are used to hold three atoms together, making them electron-deficient bonds. You encountered a similar phenomenon in the discussion of π bonding in ozone and the nitrite ion. Recall that in both these cases, we used the presence of two electrons in a π molecular orbital extending over three atoms to explain the fact that the two O–O bond distances in ozone and the two N–O bond distances in nitrite are the same, which otherwise can be explained only by the use of resonance structures.

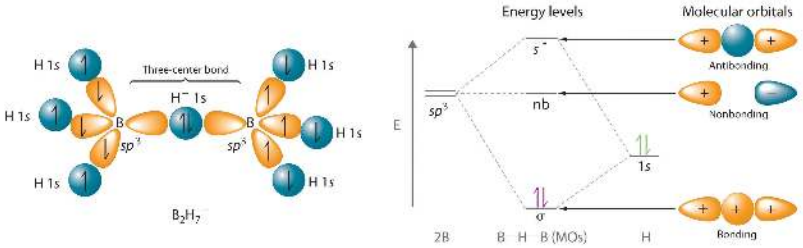



Figure 20.3.3: A Three-Center Bond Uses Two Electrons to Link Three Atoms. In the B–H–B unit shown, a hydride, with a filled 1s orbital, interacts simultaneously with empty $sp^3$ hybrids on the boron atoms of two $BH_3$ units to give three molecular orbitals. The two bonding electrons occupy the lowest-energy (σ) bonding orbital, thereby holding all three atoms together.

> *Hydrogen can lose its electron to form $H^+$, accept an electron to form $H^-$, share its electron, hydrogen bond, or form a three-center bond.*

## Synthesis, Reactions, and Compounds of Hydrogen

The first known preparation of elemental hydrogen was in 1671, when Robert Boyle dissolved iron in dilute acid and obtained a colorless, odorless, gaseous product. Hydrogen was finally identified as an element in 1766, when Henry Cavendish showed that water was the sole product of the reaction of the gas with oxygen. The explosive properties of mixtures of hydrogen with air were not discovered until early in the 18th century; they partially caused the spectacular explosion of the hydrogen-filled dirigible Hindenburg in 1937 (Figure 20.3.4). Due to its extremely low molecular mass, hydrogen gas is difficult to condense to a liquid (boiling point = 20.3 K), and solid hydrogen has one of the lowest melting points known (13.8 K).



Figure 20.3.4: The Explosive Properties of Hydrogen. When mixed with air and ignited by a spark, hydrogen gas can explode. The photograph shows the German dirigible Hindenburg on fire at Lakehurst, New Jersey, in 1937, after its hydrogen compartment was accidentally ignited as a consequence of an electrical discharge that caused the dirigible's flammable skin to catch fire.

The most common way to produce small amounts of highly pure hydrogen gas in the laboratory was discovered by Boyle: reacting an active metal (M), such as iron, magnesium, or zinc, with dilute acid:

$$M_{(s)} + 2H^{+}_{(aq)} \rightarrow H_{2(g)} + M^{2+}_{(aq)} \tag{20.3.1}$$

Hydrogen gas can also be generated by reacting metals such as aluminum or zinc with a strong base:

$$\mathrm{Al(s) + OH^{-}(aq) + 3H_2O(l) \rightarrow \frac{3}{2}H_2(g) + [Al(OH)_4]^{-}(aq)} \tag{20.3.2}$$

Solid commercial drain cleaners such as Drano use this reaction to generate gas bubbles that help break up clogs in a drainpipe. Hydrogen gas is also produced by reacting ionic hydrides with water. Because ionic hydrides are expensive, however, this reaction is generally used for only specialized purposes, such as producing HD gas by reacting a hydride with $D_2O$:

$$MH_{(s)} + D_2O(l) \rightarrow HD_{(g)} + M^{+}(aq) + OD^{-}_{(aq)} \tag{20.3.3}$$

On an industrial scale, $H_2$ is produced from methane by means of catalytic steam reforming, a method used to convert hydrocarbons to a mixture of CO and $H_2$ known as synthesis gas, or syngas. The process is carried out at elevated temperatures (800°C) in the presence of a nickel catalyst:

$$\mathrm{CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)} \tag{20.3.4}$$

Most of the elements in the periodic table form binary compounds with hydrogen, which are collectively referred to as hydrides. Binary hydrides in turn can be classified in one of three ways, each with its own characteristic properties. Covalent hydrides contain hydrogen bonded to another atom via a covalent bond or a polar covalent bond. Covalent hydrides are usually molecular substances that are relatively volatile and have low melting points. Ionic hydrides contain the hydride ion as the anion with cations derived from electropositive metals. Like most ionic compounds, they are typically nonvolatile solids that contain three-dimensional lattices of cations and anions. Unlike most ionic compounds, however, they often decompose to $H_2$(g) and the parent metal after heating. Metallic hydrides are formed by hydrogen and less electropositive metals such as the transition metals. The properties of metallic hydrides are usually similar to those of the parent metal. Consequently, metallic hydrides are best viewed as metals that contain many hydrogen atoms present as interstitial impurities.

> *Covalent hydrides are relatively volatile and have low melting points; ionic hydrides are generally nonvolatile solids in a lattice framework.*

## Summary and Key Takeaway

Hydrogen can lose an electron to form a proton, gain an electron to form a hydride ion, or form a covalent bond or polar covalent electron-pair bond. The three isotopes of hydrogen—protium ($^1$H or H), deuterium ($^2$H or D), and tritium ($^3$H or T)—have different physical properties. Deuterium and tritium can be used as tracers, substances that enable biochemists to follow the path of a molecule through an organism or a cell. Hydrogen can form compounds that contain a proton ($H^+$), a hydride ion ($H^-$), an electron-

pair bond to H, a hydrogen bond, or a three-center bond (or electron-deficient bond), in which two electrons are shared between three atoms. Hydrogen gas can be generated by reacting an active metal with dilute acid, reacting Al or Zn with a strong base, or industrially by catalytic steam reforming, which produces synthesis gas, or syngas.

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# 20.4: The Alkali Metals (Group 1)

**Learning Objectives**

1. To describe how the alkali metals are isolated.
2. To be familiar with the reactions, compounds, and complexes of the alkali metals.

The alkali metals are so reactive that they are never found in nature in elemental form. Although some of their ores are abundant, isolating them from their ores is somewhat difficult. For these reasons, the group 1 elements were unknown until the early 19th century, when Sir Humphry Davy first prepared sodium (Na) and potassium (K) by passing an electric current through molten alkalis. (The ashes produced by the combustion of wood are largely composed of potassium and sodium carbonate.) Lithium (Li) was discovered 10 years later when the Swedish chemist Johan Arfwedson was studying the composition of a new Brazilian mineral. Cesium (Cs) and rubidium (Rb) were not discovered until the 1860s, when Robert Bunsen conducted a systematic search for new elements. Known to chemistry students as the inventor of the Bunsen burner, Bunsen's spectroscopic studies of ores showed sky blue and deep red emission lines that he attributed to two new elements, Cs and Rb, respectively. Francium (Fr) is found in only trace amounts in nature, so our knowledge of its chemistry is limited. All the isotopes of Fr have very short half-lives, in contrast to the other elements in group 1.

**Humphry Davy (1778–1829)**

Davy was born in Penzance, Cornwall, England. He was a bit of a wild man in the laboratory, often smelling and tasting the products of his experiments, which almost certainly shortened his life. He discovered the physiological effects that cause nitrous oxide to be called "laughing gas" (and became addicted to it!), and he almost lost his eyesight in an explosion of nitrogen trichloride ($NCl_3$), which he was the first to prepare. Davy was one of the first to recognize the utility of Alessandro Volta's "electric piles" (batteries). By connecting several "piles" in series and inserting electrodes into molten salts of the alkali metals and alkaline earth metals, he was able to isolate six previously unknown elements as pure metals: sodium, potassium, calcium, strontium, barium, and magnesium. He also discovered boron and was the first to prepare phosphine ($PH_3$) and hydrogen telluride ($H_2Te$), both of which are highly toxic.

**Robert Wilhelm Bunsen (1811–1899)**

Bunsen was born and educated in Göttingen, Germany. His early work dealt with organic arsenic compounds, whose highly toxic nature and explosive tendencies almost killed him and did cost him an eye. He designed the Bunsen burner, a reliable gas burner, and used it and emission spectra to discover cesium (named for its blue line) and rubidium (named for its red line).

## Preparation of the Alkali Metals

Because the alkali metals are among the most potent reductants known, obtaining them in pure form requires a considerable input of energy. Pure lithium and sodium for example, are typically prepared by the electrolytic reduction of molten chlorides:

$$\mathrm{LiCl(l)} \rightarrow \mathrm{Li(l)} + \frac{1}{2}\mathrm{Cl_2(g)} \tag{20.4.1}$$

In practice, $CaCl_2$ is mixed with LiCl to lower the melting point of the lithium salt. The electrolysis is carried out in an argon atmosphere rather than the nitrogen atmosphere typically used for substances that are highly reactive with $O_2$ and water because Li reacts with nitrogen gas to form lithium nitride ($Li_3N$). Metallic sodium is produced by the electrolysis of a molten mixture of NaCl and $CaCl_2$. In contrast, potassium is produced commercially from the reduction of KCl by Na, followed by the fractional distillation of K(g). Although rubidium and cesium can also be produced by electrolysis, they are usually obtained by reacting their hydroxide salts with a reductant such as Mg:

$$2RbOH_{(s)} + Mg_{(s)} \rightarrow 2Rb_{(l)} + Mg(OH)_{2(s)} \tag{20.4.2}$$

Massive deposits of essentially pure NaCl and KCl are found in nature and are the major sources of sodium and potassium. The other alkali metals are found in low concentrations in a wide variety of minerals, but ores that contain high concentrations of these

elements are relatively rare. No concentrated sources of rubidium are known, for example, even though it is the 16th most abundant element on Earth. Rubidium is obtained commercially by isolating the 2%–4% of Rb present as an impurity in micas, minerals that are composed of sheets of complex hydrated potassium–aluminum silicates.

Alkali metals are recovered from silicate ores in a multistep process that takes advantage of the pH-dependent solubility of selected salts of each metal ion. The steps in this process are leaching, which uses sulfuric acid to dissolve the desired alkali metal ion and $Al^{3+}$ from the ore; basic precipitation to remove $Al^{3+}$ from the mixture as $Al(OH)_3$; selective precipitation of the insoluble alkali metal carbonate; dissolution of the salt again in hydrochloric acid; and isolation of the metal by evaporation and electrolysis. Figure 20.4.1 illustrates the isolation of liquid lithium from a lithium silicate ore by this process.

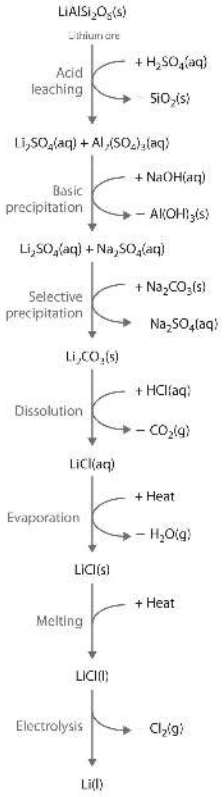



Figure 20.4.1: Isolating Lithium from Spodumene, a Lithium Silicate Ore. *The key steps are acid leaching, basic precipitation of aluminum hydroxide, selective precipitation of insoluble lithium carbonate, conversion to lithium chloride, evaporation, and electrolysis. The other alkali metals and the alkaline earth metals are recovered from their ores by similar processes.*

## General Properties of the Alkali Metals

Various properties of the group 1 elements are summarized in Table 20.4.1. In keeping with overall periodic trends, the atomic and ionic radii increase smoothly from Li to Cs, and the first ionization energies decrease as the atoms become larger. As a result of their low first ionization energies, the alkali metals have an overwhelming tendency to form ionic compounds where they have a +1 charge. All the alkali metals have relatively high electron affinities because the addition of an electron produces an anion ($M^-$) with an $ns^2$ electron configuration. The densities of the elements generally increase from Li to Cs, reflecting another common trend: because the atomic masses of the elements increase more rapidly than the atomic volumes as you go down a group, the densest elements are near the bottom of the periodic table. An unusual trend in the group 1 elements is the smooth decrease in the melting and boiling points from Li to Cs. As a result, Cs (melting point = 28.5°C) is one of only three metals (the others are Ga and Hg) that are liquids at body temperature (37°C).

Table 20.4.1: Selected Properties of the Group 1 Elements

| | Lithium | Sodium | Potassium | Rubidium | Cesium | Francium |
|---|---|---|---|---|---|---|
| atomic symbol | Li | Na | K | Rb | Cs | Fr |
| atomic number | 3 | 11 | 19 | 37 | 55 | 87 |
| atomic mass | 6.94 | 22.99 | 39.10 | 85.47 | 132.91 | 223 |
| valence electron configuration | $2s^1$ | $3s^1$ | $4s^1$ | $5s^1$ | $6s^1$ | $7s^1$ |
| melting point/boiling point (°C) | 180.5/1342 | 97.8/883 | 63.5/759 | 39.3/688 | 28.5/671 | 27/— |
| density ($g/cm^3$) at 25°C | 0.534 | 0.97 | 0.89 | 1.53 | 1.93 | — |
| atomic radius (pm) | 167 | 190 | 243 | 265 | 298 | — |
| first ionization energy (kJ/mol) | 520 | 496 | 419 | 403 | 376 | 393 |
| most common oxidation state | +1 | +1 | +1 | +1 | +1 | +1 |
| ionic radius (pm)* | 76 | 102 | 138 | 152 | 167 | — |
| electron affinity (kJ/mol) | −60 | −53 | −48 | −47 | −46 | — |
| electronegativity | 1.0 | 0.9 | 0.8 | 0.8 | 0.8 | 0.7 |
| standard electrode potential (E°, V) | −3.04 | −2.71 | −2.93 | −2.98 | −3.03 | — |
| product of reaction with $O_2$ | $Li_2O$ | $Na_2O_2$ | $KO_2$ | $RbO_2$ | $CsO_2$ | — |
| type of oxide | basic | basic | basic | basic | basic | — |
| product of reaction with $N_2$ | $Li_3N$ | none | none | none | none | — |
| product of reaction with $X_2$ | LiX | NaX | KX | RbX | CsX | — |
| product of reaction with $H_2$ | LiH | NaH | KH | RbH | CsH | — |

*The values cited are for four-coordinate ions except for $Rb^+$ and $Cs^+$, whose values are given for the six-coordinate ion.

The standard reduction potentials (E°) of the alkali metals do not follow the trend based on ionization energies. Unexpectedly, lithium is the strongest reductant, and sodium is the weakest (Table 20.4.1). Because $Li^+$ is much smaller than the other alkali metal cations, its hydration energy is the highest. The high hydration energy of $Li^+$ more than compensates for its higher ionization energy, making lithium metal the strongest reductant in aqueous solution. This apparent anomaly is an example of how the physical or the chemical behaviors of the elements in a group are often determined by the subtle interplay of opposing periodic trends.

## Reactions and Compounds of the Alkali Metals

All alkali metals are electropositive elements with an $ns^1$ valence electron configuration, forming the monocation ($M^+$) by losing the single valence electron. Because removing a second electron would require breaking into the (n − 1) closed shell, which is energetically prohibitive, the chemistry of the alkali metals is largely that of ionic compounds that contain $M^+$ ions. However, as we discuss later, the lighter group 1 elements also form a series of organometallic compounds that contain polar covalent M–C bonds.

All the alkali metals react vigorously with the halogens (group 17) to form the corresponding ionic halides, where $X$ is a halogen:

$$2M_{(s)} + X_{2(s,l,g)} \rightarrow 2M^+X^-_{(s)} \tag{20.4.3}$$

Similarly, the alkali metals react with the heavier chalcogens (sulfur, selenium, and tellurium in group 16) to produce metal chalcogenides, where Y is S, Se, or Te:

$$2M_{(s)} + Y_{(s)} \rightarrow M_2Y_{(s)} \tag{20.4.4}$$

When excess chalcogen is used, however, a variety of products can be obtained that contain chains of chalcogen atoms, such as the sodium polysulfides ($Na_2S_n$, where n = 2–6). For example, $Na_2S_3$ contains the $S_3^{2-}$ ion, which is V shaped with an S–S–S angle of about 103°. The one-electron oxidation product of the trisulfide ion ($S_3^-$) is responsible for the intense blue color of the gemstones lapis lazuli and blue ultramarine (Figure 20.4.2).

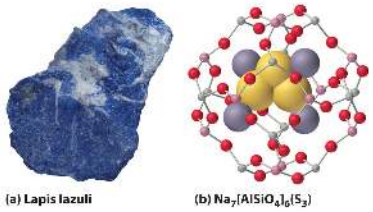



Figure 20.4.2: The Trisulfide Anion Is Responsible for the Deep Blue Color of Some Gemstones. *(a) The rich blue color of lapis lazuli is due to small amounts of the normally unstable $S_3^-$ anion. (b) The aluminosilicate cages of the minerals (zeolites) that make up the matrix of blue ultramarine stabilize the reactive anion; excess $Na^+$ ions in the structure balance the negative charges on the zeolite framework and the $S_3^-$ anion.*

Reacting the alkali metals with oxygen, the lightest element in group 16, is more complex, and the stoichiometry of the product depends on both the metal:oxygen ratio and the size of the metal atom. For instance, when alkali metals burn in air, the observed products are $Li_2O$ (white), $Na_2O_2$ (pale yellow), $KO_2$ (orange), $RbO_2$ (brown), and $CsO_2$ (orange). Only $Li_2O$ has the stoichiometry expected for a substance that contains two $M^+$ cations and one $O^{2-}$ ion. In contrast, $Na_2O_2$ contains the $O_2^{2-}$ (peroxide) anion plus two $Na^+$ cations. The other three salts, with stoichiometry $MO_2$, contain the $M^+$ cation and the $O_2^-$ (superoxide) ion. Because $O^{2-}$ is the smallest of the three oxygen anions, it forms a stable ionic lattice with the smallest alkali metal cation ($Li^+$). In contrast, the larger alkali metals—potassium, rubidium, and cesium—react with oxygen in air to give the metal superoxides. Because the $Na^+$ cation is intermediate in size, sodium reacts with oxygen to form a compound with an intermediate stoichiometry: sodium peroxide. Under specific reaction conditions, however, it is possible to prepare the oxide, peroxide, and superoxide salts of all five alkali metals, except for lithium superoxide ($LiO_2$).



A crystal of spodumene ($LiAlSi_2O_6$). This mineral is one of the most important lithium ores.

> *The chemistry of the alkali metals is largely that of ionic compounds containing the $M^+$ ions.*

The alkali metal peroxides and superoxides are potent oxidants that react, often vigorously, with a wide variety of reducing agents, such as charcoal or aluminum metal. For example, $Na_2O_2$ is used industrially for bleaching paper, wood pulp, and fabrics such as linen and cotton. In submarines, $Na_2O_2$ and $KO_2$ are used to purify and regenerate the air by removing the $CO_2$ produced by respiration and replacing it with $O_2$. Both compounds react with $CO_2$ in a redox reaction in which $O_2^{2-}$ or $O_2^-$ is simultaneously oxidized and reduced, producing the metal carbonate and $O_2$:

$$2Na_2O_{2(s)} + 2CO_{2(g)} \rightarrow 2Na_2CO_{3(s)} + O_{2(g)} \tag{20.4.5}$$

$$4KO_{2(s)} + 2CO_{2(g)} \rightarrow 2K_2CO_{3(s)} + 3O_{2(g)} \tag{20.4.6}$$

The presence of water vapor, the other product of respiration, makes $KO_2$ even more effective at removing $CO_2$ because potassium bicarbonate, rather than potassium carbonate, is formed:

$$4KO_{2(s)} + 4CO_{2(g)} + 2H_2O_{(g)} \rightarrow 4KHCO_{3(s)} + 3O_{2(g)} \tag{20.4.7}$$

Notice that 4 mol of $CO_2$ are removed in this reaction, rather than 2 mol in Equation 21.10.

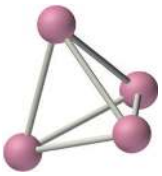
Lithium, the lightest alkali metal, is the only one that reacts with atmospheric nitrogen, forming lithium nitride ($Li_3N$). Lattice energies again explain why the larger alkali metals such as potassium do not form nitrides: packing three large $K^+$ cations around a single relatively small anion is energetically unfavorable. In contrast, all the alkali metals react with the larger group 15 elements phosphorus and arsenic to form metal phosphides and arsenides (where Z is P or As):

$$12M_{(s)} + Z_{4(s)} \rightarrow 4M_3Z_{(s)} \tag{20.4.8}$$

> *Because of lattice energies, only lithium forms a stable oxide and nitride.*

The alkali metals react with all group 14 elements, but the compositions and properties of the products vary significantly. For example, reaction with the heavier group 14 elements gives materials that contain polyatomic anions and three-dimensional cage structures, such as $K_4Si_4$ whose structure is shown here. In contrast, lithium and sodium are oxidized by carbon to produce a compound with the stoichiometry $M_2C_2$ (where M is Li or Na):

$$2M_{(s)} + 2C_{(s)} \rightarrow M_2C_{2(s)} \tag{20.4.9}$$



The three-dimensional cage structure of the $Si_4^{4-}$ ion in the ionic compound $K_4S_4$. The $Si_4^{4-}$ ion is isoelectronic and isostructural with the $P_4$ molecule.

The same compounds can be obtained by reacting the metal with acetylene ($C_2H_2$). In this reaction, the metal is again oxidized, and hydrogen is reduced:

$$2M_{(s)} + C_2H_{2(g)} \rightarrow M_2C_{2(s)} + H_{2(g)} \tag{20.4.10}$$

The acetylide ion ($C_2^{2-}$), formally derived from acetylene by the loss of both hydrogens as protons, is a very strong base. Reacting acetylide salts with water produces acetylene and MOH(aq).

The heavier alkali metals (K, Rb, and Cs) also react with carbon in the form of graphite. Instead of disrupting the hexagonal sheets of carbon atoms, however, the metals insert themselves between the sheets of carbon atoms to give new substances called **graphite intercalation compounds** (part (a) in Figure 20.4.3). The stoichiometries of these compounds include $MC_{60}$ and $MC_{48}$, which are black/gray; $MC_{36}$ and $MC_{24}$, which are blue; and $MC_8$, which is bronze (part (b) in Figure 20.4.3). The remarkably high electrical conductivity of these compounds (about 200 times greater than graphite) is attributed to a net transfer of the valence electron of the alkali metal to the graphite layers to produce, for example, $K^+C_8^-$.

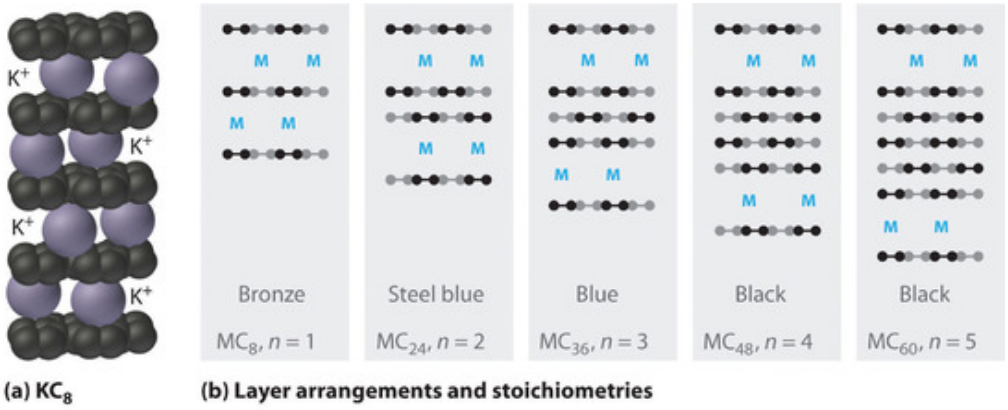



Figure 20.4.3 Graphite Intercalation Compounds. Reacting graphite with alkali metals such as K, Rb, and Cs results in partial reduction of the graphite and insertion of layers of alkali metal cations between sets of n layers of carbon atoms. (a) In $KC_8$, layers of $K^+$ ions are inserted between every pair of carbon layers, giving n = 1. (b) The stoichiometry and color of intercalation compounds depend on the number of layers of carbon atoms (n) between each layer of intercalated metal atoms. This schematic diagram illustrates the most common structures that have been observed.

All the alkali metals react directly with gaseous hydrogen at elevated temperatures to produce ionic hydrides ($M^+H^-$):

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH_{(s)} \tag{20.4.11}$$

All are also capable of reducing water to produce hydrogen gas:

$$\mathrm{M(s) + H_2O(l) \rightarrow \frac{1}{2}H_2(g) + MOH(aq)} \tag{20.4.12}$$

Although lithium reacts rather slowly with water, sodium reacts quite vigorously (Figure 20.4.4), and the heavier alkali metals (K, Rb, and Cs) react so vigorously that they invariably explode. This trend, which is not consistent with the relative magnitudes of the reduction potentials of the elements, serves as another example of the complex interplay of different forces and phenomena—in this case, kinetics and thermodynamics. Although the driving force for the reaction is greatest for lithium, the heavier metals have lower melting points. The heat liberated by the reaction causes them to melt, and the larger surface area of the liquid metal in contact with water greatly accelerates the reaction rate.

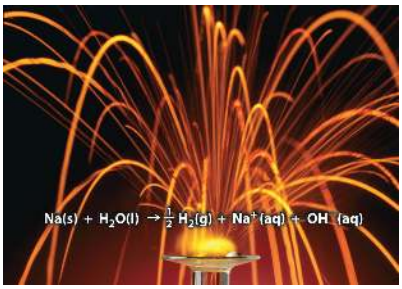



Figure 20.4.4: Reacting Sodium with Water. Like most elements in groups 1 and 2, sodium reacts violently with water. The products are the $Na^+(aq)$ ion and hydrogen gas, which is potentially explosive when mixed with air.

Alkali metal cations are found in a wide variety of ionic compounds. In general, any alkali metal salt can be prepared by reacting the alkali metal hydroxide with an acid and then evaporating the water:

$$2MOH_{(aq)} + H_2SO_{4(aq)} \rightarrow M_2SO_{4(aq)} + 2H_2O_{(l)} \tag{20.4.13}$$

$$MOH_{(aq)} + HNO_{3(aq)} \rightarrow MNO_{3(aq)} + H_2O_{(l)} \tag{20.4.14}$$

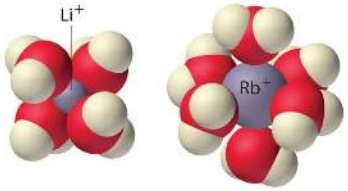
Hydroxides of alkali metals also can react with organic compounds that contain an acidic hydrogen to produce a salt. An example is the preparation of sodium acetate ($CH_3CO_2Na$) by reacting sodium hydroxide and acetic acid:

$$CH_3CO_2H_{(aq)} + NaOH_{(s)} \rightarrow CH_3CO_2Na_{(aq)} + H_2O_{(l)} \tag{20.4.15}$$

Soap is a mixture of the sodium and potassium salts of naturally occurring carboxylic acids, such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] and stearic acid [$CH_3(CH_2)_{16}CO_2H$]. Lithium salts, such as lithium stearate [$CH_3(CH_2)_{14}CO_2Li$], are used as additives in motor oils and greases.

## Complexes of the Alkali Metals

Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to react with simple Lewis bases to form metal complexes. Complex formation is most significant for the smallest cation ($Li^+$) and decreases with increasing radius. In aqueous solution, for example, $Li^+$ forms the tetrahedral $[Li(H_2O)_4]^+$ complex. In contrast, the larger alkali metal cations form octahedral $[M(H_2O)_6]^+$ complexes. Complex formation is primarily due to the electrostatic interaction of the metal cation with polar water molecules. Because of their high affinity for water, anhydrous salts that contain $Li^+$ and $Na^+$ ions (such as $Na_2SO_4$) are often used as drying agents. These compounds absorb trace amounts of water from nonaqueous solutions to form hydrated salts, which are then easily removed from the solution by filtration.




The tetrahedral $[Li(H_2O)_4]^+$ and octahedral $[Rb(H_2O)_6]^+$ complexes. The $Li^+$ ion is so small that it can accommodate only four water molecules around it, but the larger alkali metal cations tend to bind six water molecules.

> *Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to form complexes with simple Lewis bases.*

Electrostatic interactions also allow alkali metal ions to form complexes with certain cyclic polyethers and related compounds, such as crown ethers and cryptands. As discussed in Chapter 13, **crown ethers** are cyclic polyethers that contain four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms, and crown ethers with rings of different sizes prefer to bind metal ions that fit into the cavity. For example, 14-crown-4, with the smallest cavity that can accommodate a metal ion, has the highest affinity for $Li^+$, whereas 18-crown-6 forms the strongest complexes with $K^+$.

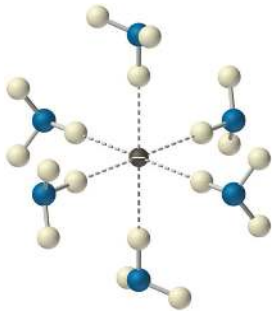
**Cryptands** are more nearly spherical analogues of crown ethers and are even more powerful and selective complexing agents. Cryptands consist of three chains containing oxygen that are connected by two nitrogen atoms (part (b) in Figure 13.7). They can completely surround (encapsulate) a metal ion of the appropriate size, coordinating to the metal by a lone pair of electrons on each O atom and the two N atoms. Like crown ethers, cryptands with different cavity sizes are highly selective for metal ions of particular sizes. Crown ethers and cryptands are often used to dissolve simple inorganic salts such as $KMnO_4$ in nonpolar organic solvents.

## Liquid Ammonia Solutions

A remarkable feature of the alkali metals is their ability to dissolve reversibly in liquid ammonia. Just as in their reactions with water, reacting alkali metals with liquid ammonia eventually produces hydrogen gas and the metal salt of the conjugate base of the solvent—in this case, the amide ion ($NH_2^-$) rather than hydroxide:

$$M(s) + NH_3(l) \rightarrow \frac{1}{2}H_2(g) + M^+(am) + NH_2^-(am) \tag{20.4.16}$$

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in Equation 21.20 tends to be rather slow. In many cases, the alkali metal amide salt ($MNH_2$) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.



Solvated electrons. The presence of solvated electrons ($e^-$, $NH_3$) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity.

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of solvated electrons ($e^-$, $NH_3$), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilized by hydrogen bonds. Alkali metal–liquid ammonia solutions of about 3 M or less are deep blue (Figure 20.4.5) and conduct electricity about 10 times better than an aqueous NaCl solution because of the high mobility of the solvated electrons. As the concentration of the metal increases above 3 M, the color changes to metallic bronze or gold, and the conductivity increases to a value comparable with that of the pure liquid metals.

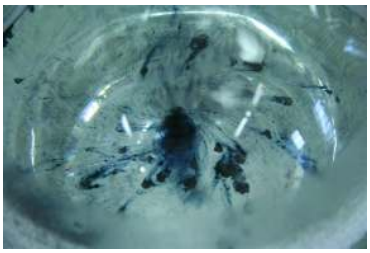


Figure 20.4.5: Alkali Metal–Liquid Ammonia Solutions. Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue color. Image copyrighted by the Klein research group.

In addition to solvated electrons, solutions of alkali metals in liquid ammonia contain the metal cation ($M^+$), the neutral metal atom (M), metal dimers ($M_2$), and the metal anion ($M^-$). The anion is formed by adding an electron to the singly occupied ns valence orbital of the metal atom. Even in the absence of a catalyst, these solutions are not very stable and eventually decompose to the thermodynamically favored products: $M^+NH_2^-$ and hydrogen gas (Equation 21.20). Nonetheless, the solvated electron is a potent reductant that is often used in synthetic chemistry.

## Organometallic Compounds of the Group 1 Elements

Compounds that contain a metal covalently bonded to a carbon atom of an organic species are called **organometallic compounds**. The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components. Because of its small size, lithium, for example, forms an extensive series of covalent organolithium compounds, such as methyllithium ($LiCH_3$), which are by far the most stable and best-known group 1 organometallic compounds. These volatile, low-melting-point solids or liquids can be sublimed or distilled at relatively low temperatures and are soluble in nonpolar solvents. Like organic compounds, the molten solids do not conduct electricity to any significant degree. Organolithium compounds have a tendency to form oligomers with the formula $(RLi)_n$, where R represents the organic component. For example, in both the solid state and solution, methyllithium exists as a tetramer with the structure shown in Figure 20.4.6, where each triangular face of the $Li_4$ tetrahedron is bridged by the carbon atom of a methyl group. Effectively, the carbon atom of each $CH_3$ group is using a single pair of electrons in an $sp^3$ hybrid lobe to bridge three lithium atoms, making this an example of two-electron, four-center bonding. Clearly, such a structure, in which each carbon atom is apparently bonded to six other atoms, cannot be explained using any of the electron-pair bonding schemes. Molecular orbital theory can explain the bonding in methyllithium, but the description is beyond the scope of this text.

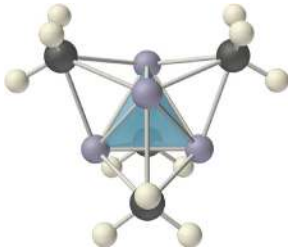


Figure 20.4.6: The Tetrameric Structure of Methyllithium. m*Methyllithium is not an ionic compound; it exists as tetrameric $(CH_3Li)_4$ molecules. The structure consists of a tetrahedral arrangement of four lithium atoms, with the carbon atom of a methyl group located above the middle of each triangular face of the tetrahedron. The carbon atoms thus bridge three lithium atoms to form four-center, two-electron bonds.*

- The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components.
- Organosodium and organopotassium compounds are more ionic than organolithium compounds. They contain discrete $M^+$ and $R^-$ ions and are insoluble or only sparingly soluble in nonpolar solvents.

## Uses of the Alkali Metals

Because sodium remains liquid over a wide temperature range (97.8–883°C), it is used as a coolant in specialized high-temperature applications, such as nuclear reactors and the exhaust valves in high-performance sports car engines. Cesium, because of its low ionization energy, is used in photosensors in automatic doors, toilets, burglar alarms, and other electronic devices. In these devices, cesium is ionized by a beam of visible light, thereby producing a small electric current; blocking the light interrupts the electric current and triggers a response.

Compounds of sodium and potassium are produced on a huge scale in industry. Each year, the top 50 industrial compounds include NaOH, used in a wide variety of industrial processes; $Na_2CO_3$, used in the manufacture of glass; $K_2O$, used in porcelain glazes; and $Na_4SiO_4$, used in detergents.

Several other alkali metal compounds are also important. For example, $Li_2CO_3$ is one of the most effective treatments available for manic depression or bipolar disorder. It appears to modulate or dampen the effect on the brain of changes in the level of neurotransmitters, which are biochemical substances responsible for transmitting nerve impulses between neurons. Consequently, patients who take “lithium” do not exhibit the extreme mood swings that characterize this disorder.

### ✔ 20.4.1

For each application, choose the more appropriate substance based on the properties and reactivities of the alkali metals and their compounds. Explain your choice in each case.

a. For a reaction that requires a strong base in a solution of tetrahydrofuran (THF), would you use LiOH or CsOH?
b. To extinguish a fire caused by burning lithium metal, would you use water, $CO_2$, $N_2$ gas, or sand ($SiO_2$)?
c. Both $LiNO_3$and $CsNO_3$ are highly soluble in acetone (2-propanone). Which of these alkali metal salts would you use to precipitate $I^-$ from an acetone solution?

**Given:** application and selected alkali metals

**Asked for:** appropriate metal for each application

**Strategy:**

Use the properties and reactivities discussed in this section to determine which alkali metal is most suitable for the indicated application.

**Solution**

a. Both LiOH and CsOH are ionic compounds that contain the hydroxide anion. $Li^+$, however, is much smaller than $Cs^+$, so the $Li^+$ cation will be more effectively solvated by the oxygen of THF with its lone pairs of electrons. This difference will have two effects: (1) LiOH is likely to be much more soluble than CsOH in the nonpolar solvent, which could be a

significant advantage, and (2) the solvated $Li^+$ ions are less likely to form tight ion pairs with the $OH^-$ ions in the relatively nonpolar solution, making the $OH^-$ more basic and thus more reactive. Thus LiOH is the better choice.

b. Lithium is a potent reductant that reacts with water to form LiOH and $H_2$ gas, so adding a source of hydrogen such as water to a lithium fire is likely to produce an explosion. Lithium also reacts with oxygen and nitrogen in the air to form $Li_2O$ and $Li_3N$, respectively, so we would not expect nitrogen to extinguish a lithium fire. Because $CO_2$ is a gaseous molecule that contains carbon in its highest accessible oxidation state (+4), adding $CO_2$ to a strong reductant such as Li should result in a vigorous redox reaction. Thus water, $N_2$, and $CO_2$ are all unsuitable choices for extinguishing a lithium fire. In contrast, sand is primarily $SiO_2$, which is a network solid that is not readily reduced. Smothering a lithium fire with sand is therefore the best choice.

c. The salt with the smaller cation has the higher lattice energy, and high lattice energies tend to decrease the solubility of a salt. However, the solvation energy of the cation is also important in determining solubility, and small cations tend to have higher solvation energies. Recall that high solvation energies tend to increase the solubility of ionic substances. Thus CsI should be the least soluble of the alkali metal iodides, and LiI the most soluble. Consequently, $CsNO_3$ is the better choice.

### ? 20.4.1

Indicate which of the alternative alkali metals or their compounds given is more appropriate for each application.

a. drying agent for an organic solvent—$Li_2SO_4$ or $Rb_2SO_4$
b. removing trace amounts of $N_2$ from highly purified Ar gas—Li, K, or Cs
c. reacting with an alkyl halide (formula RX) to prepare an organometallic compound (formula MR)—Li or K

**Answer**

a. $Li_2SO_4$
b. Li
c. Li

### ✓ 20.4.2

Predict the products of each reaction and then balance each chemical equation.

a. $Na(s) + O_2(g) \rightarrow$
b. $Li_2O(s) + H_2O(l) \rightarrow$
c. $K(s) + CH_3OH(l) \rightarrow$
d. $Li(s) + CH_3Cl(l) \rightarrow$
e. $Li_3N(s) + KCl(s) \rightarrow$

**Given:** reactants

**Asked for:** products and balanced chemical equation

**Strategy:**

**A** Determine whether one of the reactants is an oxidant or a reductant or a strong acid or a strong base. If so, a redox reaction or an acid–base reaction is likely to occur. Identify the products of the reaction.

**B** If a reaction is predicted to occur, balance the chemical equation.

**Solution**

a. **A** Sodium is a reductant, and oxygen is an oxidant, so a redox reaction is most likely. We expect an electron to be transferred from Na (thus forming $Na^+$) to $O_2$. We now need to determine whether the reduced product is a superoxide ($O_2^-$), peroxide ($O_2^{2-}$), or oxide ($O^{2-}$). Under normal reaction conditions, the product of the reaction of an alkali metal with oxygen depends on the identity of the metal. Because of differences in lattice energy, Li produces the oxide ($Li_2O$), the heavier metals (K, Rb, Cs) produce the superoxide ($MO_2$), and Na produces the peroxide ($Na_2O_2$).

**B** The balanced chemical equation is $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$.

b. **A** $Li_2O$ is an ionic salt that contains the oxide ion ($O^{2-}$), which is the completely deprotonated form of water and thus is expected to be a strong base. The other reactant, water, is both a weak acid and a weak base, so we can predict that an acid–base reaction will occur.

**B** The balanced chemical equation is $Li_2O(s) + H_2O(l) \rightarrow 2LiOH(aq)$.

c. **A** Potassium is a reductant, whereas methanol is both a weak acid and a weak base (similar to water). A weak acid produces $H^+$, which can act as an oxidant by accepting an electron to form $\frac{1}{2}H_2$. This reaction, therefore, is an acid dissociation that is driven to completion by a reduction of the protons as they are released.

**B** The balanced chemical equation is as follows: $K(s) + CH_3OH(l) \rightarrow \frac{1}{2}H_2(g) + CH_3OK(soln)$.

d. **A** One of the reactants is an alkali metal, a potent reductant, and the other is an alkyl halide. Any compound that contains a carbon–halogen bond can, in principle, be reduced, releasing a halide ion and forming an organometallic compound. That outcome seems likely in this case because organolithium compounds are among the most stable organometallic compounds known.

**B** Two moles of lithium are required to balance the equation: $2Li(s) + CH_3Cl(l) \rightarrow LiCl(s) + CH_3Li(soln)$.

e. **A** Lithium nitride and potassium chloride are largely ionic compounds. The nitride ion ($N^{3-}$) is a very strong base because it is the fully deprotonated form of ammonia, a weak acid. An acid–base reaction requires an acid as well as a base, however, and KCl is not acidic. What about a redox reaction? Both substances contain ions that have closed-shell valence electron configurations. The nitride ion could act as a reductant by donating electrons to an oxidant and forming $N_2$. KCl is not an oxidant, however, and a redox reaction requires an oxidant as well as a reductant.

**B** We conclude that the two substances will not react with each other.

**? 20.4.2**

Predict the products of each reaction and balance each chemical equation.

a. $K(s) + N_2(g) \rightarrow$
b. $Li_3N(s) + H_2O(l) \rightarrow$
c. $Na(s) + (CH_3)_2NH(soln) \rightarrow$
d. $C_6H_5Li(soln) + D_2O(l) \rightarrow C_6H_5D(l) + LiOD(soln)$
e. $CH_3CH_2Cl(soln) + 2Li \rightarrow$

**Answer**

a. no reaction
b. $Li_3N(s) + 3H_2O(l) \rightarrow NH_3(aq) + 3LiOH(aq)$
c. $Na(s) + (CH_3)_2NH(soln) \rightarrow \frac{1}{2}H_2(g) + Na[(CH_3)_2N](soln)$
d. $C_6H_5Li(soln) + D_2O(l) \rightarrow C_6H_5D(l) + LiOD(soln)$
e. $CH_3CH_2Cl(soln) + 2Li \rightarrow CH_3CH_2Li(soln) + LiCl(soln)$

## Summary

The alkali metals are potent reductants whose chemistry is largely that of ionic compounds containing the $M^+$ ion. Alkali metals have only a weak tendency to form complexes with simple Lewis bases. The first alkali metals to be isolated (Na and K) were obtained by passing an electric current through molten potassium and sodium carbonates. The alkali metals are among the most potent reductants known; most can be isolated by electrolysis of their molten salts or, in the case of rubidium and cesium, by reacting their hydroxide salts with a reductant. They can also be recovered from their silicate ores using a multistep process. Lithium, the strongest reductant, and sodium, the weakest, are examples of the physical and chemical effects of opposing periodic trends. The alkali metals react with halogens (group 17) to form ionic halides; the heavier chalcogens (group 16) to produce metal chalcogenides; and oxygen to form compounds, whose stoichiometry depends on the size of the metal atom. The peroxides and superoxides are potent oxidants. The only alkali metal to react with atmospheric nitrogen is lithium. Heavier alkali metals react with graphite to form graphite intercalation compounds, substances in which metal atoms are inserted between the sheets of carbon

atoms. With heavier group 14 elements, alkali metals react to give polyatomic anions with three-dimensional cage structures. All alkali metals react with hydrogen at high temperatures to produce the corresponding hydrides, and all reduce water to produce hydrogen gas. Alkali metal salts are prepared by reacting a metal hydroxide with an acid, followed by evaporation of the water. Both Li and Na salts are used as drying agents, compounds that are used to absorb water. Complexing agents such as crown ethers and cryptands can accommodate alkali metal ions of the appropriate size. Alkali metals can also react with liquid ammonia to form solutions that slowly decompose to give hydrogen gas and the metal salt of the amide ion ($NH_2^-$). These solutions, which contain unstable solvated electrons loosely associated with a cavity in the solvent, are intensely colored, good conductors of electricity, and excellent reductants. Alkali metals can react with organic compounds that contain an acidic proton to produce salts. They can also form organometallic compounds, which have properties that differ from those of their metallic and organic components.

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# 20.5: The Alkaline Earth Metals (Group 2)

**Learning Objectives**

- To describe how to isolate the alkaline earth metals.
- To be familiar with the reactions, compounds, and complexes of the alkaline earth metals.

Like the alkali metals, the alkaline earth metals are so reactive that they are never found in elemental form in nature. Because they form +2 ions that have very negative reduction potentials, large amounts of energy are needed to isolate them from their ores. Four of the six group 2 elements—magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba)—were first isolated in the early 19th century by Sir Humphry Davy, using a technique similar to the one he used to obtain the first alkali metals. In contrast to the alkali metals, however, compounds of the alkaline earth metals had been recognized as unique for many centuries. In fact, the name alkali comes from the Arabic al-qili, meaning “ashes,” which were known to neutralize acids. Medieval alchemists found that a portion of the ashes would melt on heating, and these substances were later identified as the carbonates of sodium and potassium ($M_2CO_3$). The ashes that did not melt (but did dissolve in acid), originally called alkaline earths, were subsequently identified as the alkaline earth oxides (MO). In 1808, Davy was able to obtain pure samples of Mg, Ca, Sr, and Ba by electrolysis of their chlorides or oxides.

Beryllium (Be), the lightest alkaline earth metal, was first obtained in 1828 by Friedrich Wöhler in Germany and simultaneously by Antoine Bussy in France. The method used by both men was reduction of the chloride by the potent “new” reductant, potassium:

$$\mathrm{BeCl_2(s) + 2K(s) \xrightarrow{\Delta} Be(s) + 2KCl(s)} \tag{20.5.1}$$

Radium was discovered in 1898 by Pierre and Marie Curie, who processed tons of residue from uranium mines to obtain about 120 mg of almost pure $RaCl_2$. Marie Curie was awarded the Nobel Prize in Chemistry in 1911 for its discovery. Because of its low abundance and high radioactivity however, radium has few uses.

## Preparation of the Alkaline Earth Metals

The alkaline earth metals are produced for industrial use by electrolytic reduction of their molten chlorides, as indicated in this equation for calcium:

$$CaCl_{2\ (l)} \rightarrow Ca_{(l)} + Cl_{2\ (g)} \tag{20.5.2}$$

The group 2 metal chlorides are obtained from a variety of sources. For example, $BeCl_2$ is produced by reacting $HCl$ with beryllia ( $BeO$), which is obtained from the semiprecious stone beryl $[Be_3Al_2(SiO_3)_6]$.



A crystal of beryl. Beryl is a gemstone and an important source of beryllium.

Chemical reductants can also be used to obtain the group 2 elements. For example, magnesium is produced on a large scale by heating a form of limestone called dolomite ($CaCO_3{\cdot}MgCO_3$) with an inexpensive iron/silicon alloy at 1150°C. Initially $CO_2$ is released, leaving behind a mixture of $CaO$ and MgO; $Mg^{2+}$ is then reduced:

$$2CaO \cdot MgO_{(s)} + Fe/Si_{(s)} \rightarrow 2Mg(l) + Ca_2SiO_{4\ (s)} + Fe(s) \tag{20.5.3}$$

An early source of magnesium was an ore called magnesite ($MgCO_3$) from the district of northern Greece called Magnesia. Strontium was obtained from strontianite ($SrCO_3$) found in a lead mine in the town of Strontian in Scotland. The alkaline earth metals are somewhat easier to isolate from their ores, as compared to the alkali metals, because their carbonate and some sulfate and hydroxide salts are insoluble.



A crystal of strontianite. Both strontianite, one of the most important strontium ores, and strontium are named after the town of Strontian, Scotland, the location of one of the first mines for strontium ores.

## General Properties of the Alkaline Earth Metals

Several important properties of the alkaline earth metals are summarized in Table 20.5.1. Although many of these properties are similar to those of the alkali metals (Table 20.5.1), certain key differences are attributable to the differences in the valence electron configurations of the two groups ($ns^2$ for the alkaline earth metals versus $ns^1$ for the alkali metals).

Table 20.5.1: Selected Properties of the Group 2 Elements

| | Beryllium | Magnesium | Calcium | Strontium | Barium | Radium |
|---|---|---|---|---|---|---|
| atomic symbol | Be | Mg | Ca | Sr | Ba | Ra |
| atomic number | 4 | 12 | 20 | 38 | 56 | 88 |
| atomic mass | 9.01 | 24.31 | 40.08 | 87.62 | 137.33 | 226 |
| valence electron configuration | $2s^2$ | $3s^2$ | $4s^2$ | $5s^2$ | $6s^2$ | $7s^2$ |
| melting point/boiling point (°C) | 1287/2471 | 650/1090 | 842/1484 | 777/1382 | 727/1897 | 700/— |
| density ($g/cm^3$) at 25°C | 1.85 | 1.74 | 1.54 | 2.64 | 3.62 | ~5 |
| atomic radius (pm) | 112 | 145 | 194 | 219 | 253 | — |
| first ionization energy (kJ/mol) | 900 | 738 | 590 | 549 | 503 | — |
| most common oxidation state | +2 | +2 | +2 | +2 | +2 | +2 |
| ionic radius (pm)* | 45 | 72 | 100 | 118 | 135 | — |
| electron affinity (kJ/mol) | ≥ 0 | ≥ 0 | −2 | −5 | −14 | — |
| electronegativity | 1.6 | 1.3 | 1.0 | 1.0 | 0.9 | 0.9 |
| standard electrode potential (E°, V) | −1.85 | −2.37 | −2.87 | −2.90 | −2.91 | −2.8 |
| product of reaction with $O_2$ | BeO | MgO | CaO | SrO | $BaO_2$ | — |
| type of oxide | amphoteric | weakly basic | basic | basic | basic | — |
| product of reaction with $N_2$ | none | $Mg_3N_2$ | $Ca_3N_2$ | $Sr_3N_2$ | $Ba_3N_2$ | — |
| product of reaction with $X_2$ | $BeX_2$ | $MgX_2$ | $CaX_2$ | $SrX_2$ | $BaX_2$ | — |
| product of reaction with $H_2$ | none | $MgH_2$ | $CaH_2$ | $SrH_2$ | $BaH_2$ | — |

*The values cited are for six-coordinate ions except for $Be^{2+}$, for which the value for the four-coordinate ion is given.

As with the alkali metals, the atomic and ionic radii of the alkaline earth metals increase smoothly from Be to Ba, and the ionization energies decrease. As we would expect, the first ionization energy of an alkaline earth metal, with an $ns^2$ valence electron configuration, is always significantly greater than that of the alkali metal immediately preceding it. The group 2 elements do exhibit some anomalies, however. For example, the density of Ca is less than that of Be and Mg, the two lightest members of the group, and Mg has the lowest melting and boiling points. In contrast to the alkali metals, the heaviest alkaline earth metal (Ba) is

the strongest reductant, and the lightest (Be) is the weakest. The standard electrode potentials of Ca and Sr are not very different from that of Ba, indicating that the opposing trends in ionization energies and hydration energies are of roughly equal importance.

One major difference between the group 1 and group 2 elements is their electron affinities. With their half-filled ns orbitals, the alkali metals have a significant affinity for an additional electron. In contrast, the alkaline earth metals generally have little or no tendency to accept an additional electron because their ns valence orbitals are already full; an added electron would have to occupy one of the vacant np orbitals, which are much higher in energy.

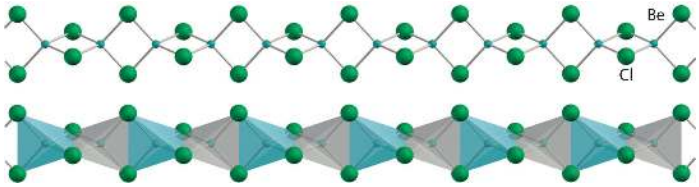
## Reactions and Compounds of the Alkaline Earth Metals

With their low first and second ionization energies, the group 2 elements almost exclusively form ionic compounds that contain $M^{2+}$ ions. As expected, however, the lightest element (Be), with its higher ionization energy and small size, forms compounds that are largely covalent. Some compounds of $Mg^{2+}$ also have significant covalent character. Hence organometallic compounds like those discussed for Li in group 1 are also important for Be and Mg in group 2.

> *The group 2 elements almost exclusively form ionic compounds containing $M^{2+}$ ions.*

All alkaline earth metals react vigorously with the halogens (group 17) to form the corresponding halides ($MX_2$). Except for the beryllium halides, these compounds are all primarily ionic in nature, containing the $M^{2+}$ cation and two $X^-$ anions. The beryllium halides, with properties more typical of covalent compounds, have a polymeric halide-bridged structure in the solid state, as shown for $BeCl_2$. These compounds are volatile, producing vapors that contain the linear X–Be–X molecules predicted by the valence-shell electron-pair repulsion (VSEPR) model. As expected for compounds with only four valence electrons around the central atom, the beryllium halides are potent Lewis acids. They react readily with Lewis bases, such as ethers, to form tetrahedral adducts in which the central beryllium is surrounded by an octet of electrons:

$$BeCl_{2(s)} + 2(CH_3CH_2)_2O_{(l)} \rightarrow BeCl_2[O(CH_2CH_3)_2]_{2(soln)} \tag{20.5.4}$$




Solid beryllium chloride ($BeCl_2$). The solid has a polymeric, halide-bridged structure.

> *Because of their higher ionization energy and small size, both Be and Mg form organometallic compounds.*

The reactions of the alkaline earth metals with oxygen are less complex than those of the alkali metals. All group 2 elements except barium react directly with oxygen to form the simple oxide MO. Barium forms barium peroxide ($BaO_2$) because the larger $O_2^{2-}$ ion is better able to separate the large $Ba^{2+}$ ions in the crystal lattice. In practice, only BeO is prepared by direct reaction with oxygen, and this reaction requires finely divided Be and high temperatures because Be is relatively inert. The other alkaline earth oxides are usually prepared by the thermal decomposition of carbonate salts:

$$\mathrm{MCO_3(s) \xrightarrow{\Delta} MO(s) + CO_2(g)} \tag{20.5.5}$$

The reactions of the alkaline earth metals with the heavier chalcogens (Y) are similar to those of the alkali metals. When the reactants are present in a 1:1 ratio, the binary chalcogenides (MY) are formed; at lower M:Y ratios, salts containing polychalcogenide ions ($Y_n^{2-}$) are formed.

In the reverse of Equation 20.5.5, the oxides of Ca, Sr, and Ba react with $CO_2$ to regenerate the carbonate. Except for BeO, which has significant covalent character and is therefore amphoteric, all the alkaline earth oxides are basic. Thus they react with water to form the hydroxides—$M(OH)_2$:

$$MO_{(s)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{20.5.6}$$

and they dissolve in aqueous acid. Hydroxides of the lighter alkaline earth metals are insoluble in water, but their solubility increases as the atomic number of the metal increases. Because BeO and MgO are much more inert than the other group 2 oxides, they are used as refractory materials in applications involving high temperatures and mechanical stress. For example, MgO (melting point = 2825°C) is used to coat the heating elements in electric ranges.

The carbonates of the alkaline earth metals also react with aqueous acid to give $CO_2$ and $H_2O$:

$$MCO_{3(s)} + 2H^+_{(aq)} \rightarrow M^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{20.5.7}$$

The reaction in Equation 20.5.7 is the basis of antacids that contain $MCO_3$, which is used to neutralize excess stomach acid.

The trend in the reactivities of the alkaline earth metals with nitrogen is the opposite of that observed for the alkali metals. Only the lightest element (Be) does not react readily with $N_2$ to form the nitride ($M_3N_2$), although finely divided Be will react at high temperatures. The higher lattice energy due to the highly charged $M^{2+}$ and $N^{3-}$ ions is apparently sufficient to overcome the chemical inertness of the $N_2$ molecule, with its N≡N bond. Similarly, all the alkaline earth metals react with the heavier group 15 elements to form binary compounds such as phosphides and arsenides with the general formula $M_3Z_2$.

> *Higher lattice energies cause the alkaline earth metals to be more reactive than the alkali metals toward group 15 elements.*

When heated, all alkaline earth metals, except for beryllium, react directly with carbon to form ionic carbides with the general formula $MC_2$. The most important alkaline earth carbide is calcium carbide ($CaC_2$), which reacts readily with water to produce acetylene. For many years, this reaction was the primary source of acetylene for welding and lamps on miners' helmets. In contrast, beryllium reacts with elemental carbon to form $Be_2C$, which formally contains the $C^{4-}$ ion (although the compound is covalent). Consistent with this formulation, reaction of $Be_2C$ with water or aqueous acid produces methane:

$$Be_2C_{(s)} + 4H_2O_{(l)} \rightarrow 2Be(OH)_{2(s)} + CH_{4(g)} \tag{20.5.8}$$

Beryllium does not react with hydrogen except at high temperatures (1500°C), although $BeH_2$ can be prepared at lower temperatures by an indirect route. All the heavier alkaline earth metals (Mg through Ba) react directly with hydrogen to produce the binary hydrides ($MH_2$). The hydrides of the heavier alkaline earth metals are ionic, but both $BeH_2$ and $MgH_2$ have polymeric structures that reflect significant covalent character. All alkaline earth hydrides are good reducing agents that react rapidly with water or aqueous acid to produce hydrogen gas:

$$CaH_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + 2H_{2(g)} \tag{20.5.9}$$

Like the alkali metals, the heavier alkaline earth metals are sufficiently electropositive to dissolve in liquid ammonia. In this case, however, two solvated electrons are formed per metal atom, and no equilibriums involving metal dimers or metal anions are known. Also, like the alkali metals, the alkaline earth metals form a wide variety of simple ionic salts with oxoanions, such as carbonate, sulfate, and nitrate. The nitrate salts tend to be soluble, but the carbonates and sulfates of the heavier alkaline earth metals are quite insoluble because of the higher lattice energy due to the doubly charged cation and anion. The solubility of the carbonates and the sulfates decreases rapidly down the group because hydration energies decrease with increasing cation size.

> *The solubility of alkaline earth carbonate and sulfates decrease down the group because the hydration energies decrease.*

## Complexes of the Alkaline Earth Metals

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases than do the alkali metals. This tendency is most important for the lightest cation ($Be^{2+}$) and decreases rapidly with the increasing radius of the metal ion.

> *The alkaline earth metals have a substantially greater tendency to form complexes with Lewis bases than do the alkali metals.*

The chemistry of $Be^{2+}$ is dominated by its behavior as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, $Be^{2+}$ salts dissolve in water to form acidic solutions that contain the tetrahedral

$[Be(H_2O)_4]^{2+}$ ion. Because of its high charge-to-radius ratio, the $Be^{2+}$ ion polarizes coordinated water molecules, thereby increasing their acidity:

$$[Be(H_2O)_4]^{2+}_{(aq)} \rightarrow [Be(H_2O)_3(OH)]^{+}_{(aq)} + H^{+}_{(aq)} \tag{20.5.10}$$

Similarly, in the presence of a strong base, beryllium and its salts form the tetrahedral hydroxo complex: $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex: $[BeF_4]^{2-}$. Recall that beryllium halides behave like Lewis acids by forming adducts with Lewis bases (Equation 20.5.4).

The heavier alkaline earth metals also form complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations ($Mg^{2+}$ and $Ca^{2+}$). Thus aqueous solutions of $Mg^{2+}$ contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. Like the alkali metals, the alkaline earth metals form complexes with neutral cyclic ligands like the crown ethers and cryptands discussed in Section 21.3.

## Organometallic Compounds Containing Group 2 Elements

Like the alkali metals, the lightest alkaline earth metals (Be and Mg) form the most covalent-like bonds with carbon, and they form the most stable organometallic compounds. Organometallic compounds of magnesium with the formula RMgX, where R is an alkyl or aryl group and X is a halogen, are universally called Grignard reagents, after Victor Grignard (1871–1935), the French chemist who discovered them. Grignard reagents can be used to synthesize various organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids, esters, thiols, and amines.

## Uses of the Alkaline Earth Metals

Elemental magnesium is the only alkaline earth metal that is produced on a large scale (about $5 \times 10^5$ tn per year). Its low density (1.74 g/cm$^3$ compared with 7.87 g/cm$^3$ for iron and 2.70 g/cm$^3$ for aluminum) makes it an important component of the lightweight metal alloys used in aircraft frames and aircraft and automobile engine parts (Figure 20.5.1). Most commercial aluminum actually contains about 5% magnesium to improve its corrosion resistance and mechanical properties. Elemental magnesium also serves as an inexpensive and powerful reductant for the production of a number of metals, including titanium, zirconium, uranium, and even beryllium, as shown in the following equation:

$$TiCl_{4\ (l)} + 2Mg(s) \rightarrow Ti_{(s)} + 2MgCl_{2\ (s)} \tag{20.5.11}$$

The only other alkaline earth that is widely used as the metal is beryllium, which is extremely toxic. Ingestion of beryllium or exposure to beryllium-containing dust causes a syndrome called berylliosis, characterized by severe inflammation of the respiratory tract or other tissues. A small percentage of beryllium dramatically increases the strength of copper or nickel alloys, which are used in nonmagnetic, nonsparking tools (such as wrenches and screwdrivers), camera springs, and electrical contacts. The low atomic number of beryllium gives it a very low tendency to absorb x-rays and makes it uniquely suited for applications involving radioactivity. Both elemental Be and BeO, which is a high-temperature ceramic, are used in nuclear reactors, and the windows on all x-ray tubes and sources are made of beryllium foil.



Figure 20.5.1: Magnesium Alloys Are Lightweight and Corrosion Resistant. Because magnesium is about five times lighter than steel and 50% lighter than aluminum, it was long considered the “material of the future,” as shown in this 1950 concept Buick LeSabre sports car made almost entirely of magnesium and aluminum alloys. Modern aluminum alloys usually contain about 5% magnesium to improve their corrosion resistance and mechanical properties.

Millions of tons of calcium compounds are used every year. As discussed in earlier chapters, $CaCl_2$ is used as "road salt" to lower the freezing point of water on roads in cold temperatures. In addition, $CaCO_3$ is a major component of cement and an ingredient in many commercial antacids. "Quicklime" (CaO), produced by heating $CaCO_3$ (Equation 20.5.5), is used in the steel industry to remove oxide impurities, make many kinds of glass, and neutralize acidic soil. Other applications of group 2 compounds described in earlier chapters include the medical use of $BaSO_4$ in "barium milkshakes" for identifying digestive problems by x-rays and the use of various alkaline earth compounds to produce the brilliant colors seen in fireworks.

### Example 20.5.1

For each application, choose the most appropriate substance based on the properties and reactivities of the alkaline earth metals and their compounds. Explain your choice in each case. Use any tables you need in making your decision, such as $K_{sp}$ values (Table 17.1), lattice energies (Table 8.1), and band-gap energies.

a. To neutralize excess stomach acid that causes indigestion, would you use $BeCO_3$, $CaCO_3$, or $BaCO_3$?
b. To remove $CO_2$ from the atmosphere in a space capsule, would you use MgO, CaO, or BaO?
c. As a component of the alloy in an automotive spark plug electrode, would you use Be, Ca, or Ba?

**Given:** application and selected alkaline earth metals

**Asked for:** most appropriate substance for each application

**Strategy:**

Based on the discussion in this section and any relevant information elsewhere in this book, determine which substance is most appropriate for the indicated use.

**Solution**

a. All the alkaline earth carbonates will neutralize an acidic solution by Equation 20.5.7. Because beryllium and its salts are toxic, however, $BeCO_3$ cannot be used as an antacid. Of the remaining choices, $CaCO_3$ is somewhat more soluble than $BaCO_3$ (according to the $K_{sp}$ values in Table 17.1), suggesting that it will act more rapidly. Moreover, the formula mass of $CaCO_3$ is 100.1 amu, whereas that of $BaCO_3$ is almost twice as large. Therefore, neutralizing a given amount of acid would require twice the mass of $BaCO_3$ compared with $CaCO_3$. Furthermore, reaction of $BaCO_3$ with acid produces a solution containing $Ba^{2+}$ ions, which are toxic. ($Ba^{2+}$ is a stimulant that can cause ventricular fibrillation of the heart.) Finally, $CaCO_3$ is produced on a vast scale, so $CaCO_3$ is likely to be significantly less expensive than any barium compound. Consequently, $CaCO_3$ is the best choice for an antacid.
b. This application involves reacting $CO_2$ with an alkaline earth oxide to form the carbonate, which is the reverse of the thermal decomposition reaction in which $MCO_3$ decomposes to $CO_2$ and the metal oxide MO (Equation 20.5.5). Owing to their higher lattice energies, the smallest alkaline earth metals should form the most stable oxides. Hence their carbonates should decompose at the lowest temperatures, as is observed ($BeCO_3$ decomposes at 100°C; $BaCO_3$ at 1360°C). If the carbonate with the smallest alkaline earth metal decomposes most readily, we would expect the reverse reaction (formation of a carbonate) to occur most readily with the largest metal cation ($Ba^{2+}$). Hence BaO is the best choice.
c. The alloy in a spark plug electrode must release electrons and promote their flow across the gap between the electrodes at high temperatures. Of the three metals listed, Ba has the lowest ionization energy and thus releases electrons most readily. Heating a barium-containing alloy to high temperatures will cause some ionization to occur, providing the initial step in forming a spark.

### Exercise 20.5.1

Which of the indicated alkaline earth metals or their compounds is most appropriate for each application?

a. drying agent for removing water from the atmosphere—$CaCl_2$, $MgSO_4$, or $BaF_2$
b. removal of scale deposits (largely $CaCO_3$) in water pipes—HCl(aq) or $H_2SO_4$(aq)
c. removal of traces of $N_2$ from purified argon gas—Be, Ca, or Ba

**Answer**

a. $MgSO_4$
b. HCl
c. Ba

## Example 20.5.2

Predict the products of each reaction and then balance each chemical equation.

a. CaO(s) + HCl(g) →
b. MgO(s) + excess $OH^-$(aq) →
c. $CaH_2(s) + TiO_2(s) \xrightarrow{\Delta}$

**Given:** reactants

**Asked for:** products and balanced chemical equation

**Strategy:**

Follow the procedure given in Example 3 to predict the products of each reaction and then balance each chemical equation.

**Solution**

a. **A** Gaseous HCl is an acid, and CaO is a basic oxide that contains the $O^{2-}$ ion. This is therefore an acid–base reaction that produces $CaCl_2$ and $H_2O$.

**B** The balanced chemical equation is

$$CaO_{(s)} + 2HCl_{(g)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} \tag{20.5.12}$$

b. **A** Magnesium oxide is a basic oxide, so it can either react with water to give a basic solution or dissolve in an acidic solution. Hydroxide ion is also a base. Because we have two bases but no acid, an acid–base reaction is impossible. A redox reaction is not likely because MgO is neither a good oxidant nor a good reductant.

**B** We conclude that no reaction occurs.

c. **A** Because $CaH_2$ contains the hydride ion ($H^-$), it is a good reductant. It is also a strong base because $H^-$ ions can react with $H^+$ ions to form $H_2$. Titanium oxide ($TiO_2$) is a metal oxide that contains the metal in its highest oxidation state (+4 for a group 4 metal); it can act as an oxidant by accepting electrons. We therefore predict that a redox reaction will occur, in which $H^-$ is oxidized and $Ti^{4+}$ is reduced. The most probable reduction product is metallic titanium, but what is the oxidation product? Oxygen must appear in the products, and both CaO and $H_2O$ are stable compounds. The +1 oxidation state of hydrogen in $H_2O$ is a sign that an oxidation has occurred ($2H^- \rightarrow 2H^+ + 4e^-$).

**B** The balanced chemical equation is

$$CaH_2(s) + TiO_2(s) \xrightarrow{\Delta} Ti(s) + CaO(s) + H_2O(l)$$

We could also write the products as Ti(s) + $Ca(OH)_2$(s).

## Exercise 20.5.2

Predict the products of each reaction and then balance each chemical equation.

a. $BeCl_2(s) + Mg(s) \xrightarrow{\Delta}$
b. $BaCl_2$(aq) + $Na_2SO_4$(aq) →
c. BeO(s) + $OH^-$(aq) + $H_2O$(l) →

**Answer**

a. $BeCl_2(s) + Mg(s) \xrightarrow{\Delta} Be(s) + MgCl_2(s)$
b. $BaCl_2$(aq) + $Na_2SO_4$(aq) → $BaSO_4$(s) + 2NaCl(aq)
c. BeO(s) + $2OH^-$(aq) + $H_2O$(l) → $[Be(OH)_4]^{2-}$(aq)

## Summary

Group 2 elements almost exclusively form ionic compounds containing the $M^{2+}$ ion, they are more reactive toward group 15 elements, and they have a greater tendency to form complexes with Lewis bases than do the alkali metals. Pure samples of most of the alkaline earth metals can be obtained by electrolysis of the chlorides or oxides. Beryllium was first obtained by the reduction of its chloride; radium chloride, which is radioactive, was obtained through a series of reactions and separations. In contrast to the alkali metals, the alkaline earth metals generally have little or no affinity for an added electron. All alkaline earth metals react with the halogens to produce the corresponding halides, with oxygen to form the oxide (except for barium, which forms the peroxide), and with the heavier chalcogens to form chalcogenides or polychalcogenide ions. All oxides except BeO react with $CO_2$ to form carbonates, which in turn react with acid to produce $CO_2$ and $H_2O$. Except for Be, all the alkaline earth metals react with $N_2$ to form nitrides, and all react with carbon and hydrogen to form carbides and hydrides. Alkaline earth metals dissolve in liquid ammonia to give solutions that contain two solvated electrons per metal atom. The alkaline earth metals have a greater tendency than the alkali metals to form complexes with crown ethers, cryptands, and other Lewis bases. The most important alkaline earth organometallic compounds are Grignard reagents (RMgX), which are used to synthesize organic compounds.

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# 20.6: The s-Block Elements in Biology

**Learning Objectives**

- To be familiar with the roles of the *s*-block elements in biology.

The *s*-block elements play important roles in biological systems. Covalent hydrides, for example, are the building blocks of organic compounds, and other compounds and ions containing *s*-block elements are found in tissues and cellular fluids. In this section, we describe some ways in which biology depends on the properties of the group 1 and group 2 elements.

## Covalent Hydrides

There are three major classes of hydrides—covalent, ionic, and metallic—but only covalent hydrides occur in living cells and have any biochemical significance. As you learned in Chapter 3 , carbon and hydrogen have similar electronegativities, and the C–H bonds in organic molecules are strong and essentially nonpolar. Little acid–base chemistry is involved in the cleavage or formation of these bonds. In contrast, because hydrogen is less electronegative than oxygen and nitrogen (symbolized by Z), the H–Z bond in the hydrides of these elements is polarized ($H^{\delta+}$–$Z^{\delta-}$). Consequently, the hydrogen atoms in these H–Z bonds are relatively acidic. Moreover, S–H bonds are relatively weak due to poor *s* orbital overlap, so they are readily cleaved to give a proton. Hydrides in which H is bonded to O, N, or S atoms are therefore polar, hydrophilic molecules that form hydrogen bonds. They also undergo acid–base reactions by transferring a proton.

### Note the Pattern

Covalent hydrides in which H is bonded to O, N, or S atoms are polar and hydrophilic, form hydrogen bonds, and transfer a proton in their acid-base reactions.

Hydrogen bonds are crucial in biochemistry, in part because they help hold proteins in their biologically active folded structures. Hydrogen bonds also connect the two intertwining strands of DNA (deoxyribonucleic acid), the substance that contains the genetic code for all organisms. (For more information on DNA, see Section 23.6 .) Because hydrogen bonds are easier to break than the covalent bonds that form the individual DNA strands, the two intertwined strands can be separated to give intact single strands, which is essential for the duplication of genetic information.

In addition to the importance of hydrogen bonds in biochemical molecules, the extensive hydrogen-bonding network in water is one of the keys to the existence of life on our planet. Based on its molecular mass, water should be a gas at room temperature (20°C), but the strong intermolecular interactions in liquid water greatly increase its boiling point. Hydrogen bonding also produces the relatively open molecular arrangement found in ice, which causes ice to be less dense than water. Because ice floats on the surface of water, it creates an insulating layer that allows aquatic organisms to survive during cold winter months.

These same strong intermolecular hydrogen-bonding interactions are also responsible for the high heat capacity of water and its high heat of fusion. A great deal of energy must be removed from water for it to freeze. Consequently, as noted in Chapter 9, large bodies of water act as “thermal buffers” that have a stabilizing effect on the climate of adjacent land areas. Perhaps the most striking example of this effect is the fact that humans can live comfortably at very high latitudes. For example, palm trees grow in southern England at the same latitude (51°N) as the southern end of frigid Hudson Bay and northern Newfoundland in North America, areas known more for their moose populations than for their tropical vegetation. Warm water from the Gulf Stream current in the Atlantic Ocean flows clockwise from the tropical climate at the equator past the eastern coast of the United States and then turns toward England, where heat stored in the water is released. The temperate climate of Europe is largely attributable to the thermal properties of water.

### Note the Pattern

Strong intermolecular hydrogen-bonding interactions are responsible for the high heat capacity of water and its high heat of fusion.

## Macrominerals

The members of group 1 and group 2 that are present in the largest amounts in organisms are sodium, potassium, magnesium, and calcium, all of which form monatomic cations with a charge of +1 (group 1, $M^+$) or +2 (group 2, $M^{2+}$). Biologically, these elements

can be classified as *macrominerals*.

For example, calcium is found in the form of relatively insoluble calcium salts that are used as structural materials in many organisms. Hydroxyapatite [$Ca_5(PO_4)_3OH$] is the major component of bones, calcium carbonate ($CaCO_3$) is the major component of the shells of mollusks and the eggs of birds and reptiles, and calcium oxalate ($CaO_2CCO_2$) is found in many plants. Because calcium and strontium have similar sizes and charge-to-radius ratios, small quantities of strontium are always found in bone and other calcium-containing structural materials. Normally this is not a problem because the $Sr^{2+}$ ions occupy sites that would otherwise be occupied by $Ca^{2+}$ ions. When trace amounts of radioactive $^{90}Sr$ are released into the atmosphere from nuclear weapons tests or a nuclear accident, however, the radioactive strontium eventually reaches the ground, where it is taken up by plants that are consumed by dairy cattle. The isotope then becomes concentrated in cow's milk, along with calcium. Because radioactive strontium coprecipitates with calcium in the hydroxyapatite that surrounds the bone marrow (where white blood cells are produced), children, who typically ingest more cow's milk than adults, are at substantially increased risk for leukemia, a type of cancer characterized by the overproduction of white blood cells.

## Ion Transport

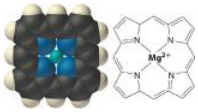
The $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ ions are important components of intracellular and extracellular fluids. Both $Na^+$ and $Ca^{2+}$ are found primarily in *extra*cellular fluids, such as blood plasma, whereas $K^+$ and $Mg^{2+}$ are found primarily in *intra*cellular fluids. Substantial inputs of energy are required to establish and maintain these concentration gradients and prevent the system from reaching equilibrium. Thus energy is needed to transport each ion across the cell membrane toward the side with the higher concentration. The biological machines that are responsible for the selective transport of these metal ions are complex assemblies of proteins called ion pumpsA complex assembly of proteins that selectively transport ions across cell membranes by their high affinity for ions of a certain charge and radius.. Ion pumps recognize and discriminate between metal ions in the same way that crown ethers and cryptands do, with a high affinity for ions of a certain charge and radius.

Defects in the ion pumps or their control mechanisms can result in major health problems. For example, *cystic fibrosis*, the most common inherited disease in the United States, is caused by a defect in the transport system (in this case, chloride ions). Similarly, in many cases, *hypertension*, or high blood pressure, is thought to be due to defective $Na^+$ uptake and/or excretion. If too much $Na^+$ is absorbed from the diet (or if too little is excreted), water diffuses from tissues into the blood to dilute the solution, thereby decreasing the osmotic pressure in the circulatory system. The increased volume increases the blood pressure, and ruptured arteries called *aneurysms* can result, often in the brain. Because high blood pressure causes other medical problems as well, it is one of the most important biomedical disorders in modern society.

For patients who suffer from hypertension, low-sodium diets that use NaCl substitutes, such as KCl, are often prescribed. Although KCl and NaCl give similar flavors to foods, the $K^+$ is not readily taken up by the highly specific $Na^+$-uptake system. This approach to controlling hypertension is controversial, however, because direct correlations between dietary $Na^+$ content and blood pressure are difficult to demonstrate in the general population. More important, recent observations indicate that high blood pressure may correlate more closely with inadequate intake of calcium in the diet than with excessive sodium levels. This finding is important because the typical "low-sodium" diet is also low in good sources of calcium, such as dairy products.

Some of the most important biological functions of the group 1 and group 2 metals are due to small changes in the cellular concentrations of the metal ion. The transmission of nerve impulses, for example, is accompanied by an increased flux of $Na^+$ ions into a nerve cell. Similarly, the binding of various hormones to specific receptors on the surface of a cell leads to a rapid influx of $Ca^{2+}$ ions; the resulting sudden rise in the intracellular $Ca^{2+}$ concentration triggers other events, such as muscle contraction, the release of neurotransmitters, enzyme activation, or the secretion of other hormones.

Within cells, $K^+$ and $Mg^{2+}$ often activate particular enzymes by binding to specific, negatively charged sites in the enzyme structure. *Chlorophyll*, the green pigment used by all plants to absorb light and drive the process of *photosynthesis*, contains magnesium. During photosynthesis, $CO_2$ is reduced to form sugars such as glucose. The structure of the central portion of a chlorophyll molecule resembles a crown ether (part (a) in Figure 13.2.4) with four five-member nitrogen-containing rings linked together to form a large ring that provides a "hole" the proper size to tightly bind $Mg^{2+}$.



**The structure of the central core of chlorophyll, a magnesium complex present in all photosynthetic tissues.** Note the resemblance to the crown ether complexes discussed in Chapter 13.

## Ionophores

Because the health of cells depends on maintaining the proper levels of cations in intracellular fluids, any change that affects the normal flux of metal ions across cell membranes could well cause an organism to die. Molecules that facilitate the transport of metal ions across membranes are generally called ionophoresA molecule that facilitates the transport of metal ions across membranes. (*ion* plus *phore* from the Greek *phorein*, meaning "to carry"). Many ionophores are potent antibiotics that can kill or inhibit the growth of bacteria. An example is *valinomycin*, a cyclic molecule with a central cavity lined with oxygen atoms (part (a) in Figure 20.5.1) that is similar to the cavity of a crown ether (part (a) in Figure 13.2.4). Like a crown ether, valinomycin is highly selective: its affinity for $K^+$ is about 1000 times greater than that for $Na^+$. By increasing the flux of $K^+$ ions into cells, valinomycin disrupts the normal $K^+$ gradient across a cell membrane, thereby killing the cell (part (b) in Figure 20.5.1).

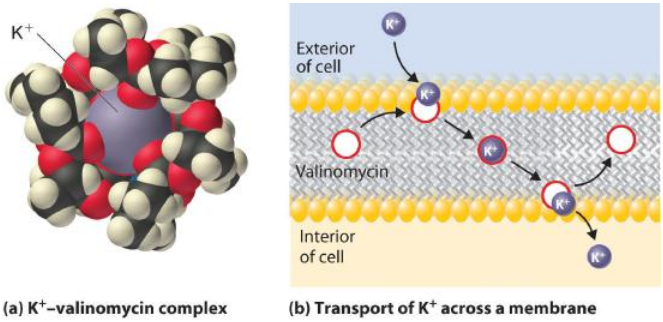



Figure 20.5.1 Valinomycin Is an Antibiotic That Functions Like an Ionophore (a) This model of the structure of the $K^+$–valinomycin complex, determined by x-ray diffraction, shows how the valinomycin molecule wraps itself around the $K^+$ ion, shielding it from the environment, in a manner reminiscent of a crown ether complex. (For more information on the crown ethers, see Section 13.2 .) (b) Valinomycin kills bacteria by facilitating the transport of $K^+$ ions across the cell membrane, thereby disrupting the normal distribution of ions in the bacterium. At the surface of the membrane, valinomycin binds a $K^+$ ion. Because the hydrophobic exterior of the valinomycin molecule forms a "doughnut" that shields the positive charge of the metal ion, the $K^+$–valinomycin complex is highly soluble in the nonpolar interior of the membrane. After the $K^+$–valinomycin complex diffuses across the membrane to the interior of the cell, the $K^+$ ion is released, and the valinomycin is free to diffuse back to the other side of the membrane to bind another $K^+$ ion. Valinomycin thereby destroys the normal $K^+$ gradient across the membrane, killing the cell.

### Example 20.5.1

A common way to study the function of a metal ion in biology is to replace the naturally occurring metal with one whose reactivity can be traced by spectroscopic methods. The substitute metal ion must bind to the same site as the naturally occurring ion, and it must have a similar (or greater) affinity for that site, as indicated by its charge density. Arrange the following ions in order of increasing effectiveness as a replacement for $Ca^{2+}$, which has an ionic radius of 100 pm (numbers in parentheses are ionic radii): $Na^+$ (102 pm), $Eu^{2+}$ (117 pm), $Sr^{2+}$ (118 pm), $F^-$ (133 pm), $Pb^{2+}$ (119 pm), and $La^{3+}$ (103 pm). Explain your reasoning.

**Given:** ions and ionic radii

**Asked for:** suitability as replacement for $Ca^{2+}$

**Strategy:**

Use periodic trends to arrange the ions from least effective to most effective as a replacement for $Ca^{2+}$.

**Solution:**

The most important properties in determining the affinity of a biological molecule for a metal ion are the size and charge-to-radius ratio of the metal ion. Of the possible $Ca^{2+}$ replacements listed, the $F^-$ ion has the opposite charge, so it should have no affinity for a $Ca^{2+}$-binding site. $Na^+$ is approximately the right size, but with a +1 charge it will bind much more weakly than $Ca^{2+}$. Although

$Eu^{2+}$, $Sr^{2+}$, and $Pb^{2+}$ are all a little larger than $Ca^{2+}$, they are probably similar enough in size and charge to bind. Based on its ionic radius, $Eu^{2+}$ should bind most tightly of the three. $La^{3+}$ is nearly the same size as $Ca^{2+}$ and more highly charged. With a higher charge-to-radius ratio and a similar size, $La^{3+}$ should bind tightly to a $Ca^{2+}$ site and be the most effective replacement for $Ca^{2+}$. The order is $F^- << Na^+ << Pb^{2+} \sim Sr^{2+} \sim Eu^{2+} < La^{3+}$.

Exercise

The ionic radius of $K^+$ is 138 pm. Arrange the following ions in order of increasing affinity for a $K^+$-binding site in an enzyme (numbers in parentheses are ionic radii): $Na^+$ (102 pm), $Rb^+$ (152 pm), $Ba^{2+}$ (135 pm), $Cl^-$ (181 pm), and $Tl^+$ (150 pm).

**Answer** $Cl^- << Na^+ < Tl^+ \sim Rb^+ < Ba^{2+}$

## Summary

Covalent hydrides in which hydrogen is bonded to oxygen, nitrogen, or sulfur are polar, hydrophilic molecules that form hydrogen bonds and undergo acid–base reactions. Hydrogen-bonding interactions are crucial in stabilizing the structure of proteins and DNA and allow genetic information to be duplicated. The hydrogen-bonding interactions in water and ice also allow life to exist on our planet. The group 1 and group 2 metals present in organisms are *macrominerals*, which are important components of intracellular and extracellular fluids. Small changes in the cellular concentration of a metal ion can have a significant impact on biological functions. Metal ions are selectively transported across cell membranes by **ion pumps**, which bind ions based on their charge and radius. **Ionophores**, many of which are potent antibiotics, facilitate the transport of metal ions across membranes.

## Key Takeaway

- Among their many roles in biology, the *s*-block elements allow genetic information to be duplicated and are important components of intracellular and extracellular fluids.

## Conceptual Problems

1. Explain the thermochemical properties of water in terms of its intermolecular bonding interactions. How does this affect global climate patterns?
2. Of the three classes of hydrides, which is (are) biochemically significant? How do you account for this?
3. Many proteins are degraded and become nonfunctional when heated higher than a certain temperature, even though the individual protein molecules do not undergo a distinct chemical change. Propose an explanation for this observation.
4. Los Angeles has moderate weather throughout the year, with average temperatures between 57°F and 70°F. In contrast, Palm Springs, which is just 100 miles inland, has average temperatures between 55°F and 95°F. Explain the difference in the average temperature ranges between the two cities.
5. Although all group 1 ions have the same charge (+1), $Na^+$ and $K^+$ ions are selectively transported across cell membranes. What strategy do organisms employ to discriminate between these two cations?

## Structure and Reactivity

1. A 0.156 g sample of a chloride salt of an alkaline earth metal is dissolved in enough water to make 20.5 mL of solution. If this solution has an osmotic pressure of 2.68 atm at 25°C, what is the identity of the alkaline earth metal?
2. The thermal buffering capacity of water is one of the reasons the human body is capable of withstanding a wide range of temperatures. How much heat (in kilojoules) is required to raise the temperature of a 70.0 kg human from 37.0°C to 38.0°C? Assume that 70% of the mass of the body is water and that body fluids have the same specific heat as water.
3. During illness, body temperature can increase by more than 2°C. One piece of folklore is that you should “feed a fever.” Using the data in Table 8.7.2, how many fried chicken drumsticks would a 70.0 kg person need to eat to generate a 2.0°C change in body temperature? Assume the following: there is complete conversion of the caloric content of the chicken to thermal energy, 70% of the mass of the body is solely due to water, and body fluids have the same specific heat as water.
4. Hydrogen bonding is partly responsible for the high enthalpy of vaporization of water ($\Delta H_{vap}$ = 43.99 kJ/mol at 25°C), which contributes to cooling the body during exercise. Assume that a 50.0 kg runner produces 20.0 g of perspiration during a race, and

all the perspiration is converted to water vapor at 37.0°C. What amount of heat (in joules) is removed from the runner's skin if the perspiration consists of only water?

## Answer

1. Ba
2.
3.
4.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 20.E: Periodic Trends and the s-Block Elements (Exercises)

A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: Principles, Patterns, and Applications**

by Bruce A. Averill



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These are homework exercises to accompany the Textmap created for "Chemistry: Principles, Patterns, and Applications" by Bruce A. Averill and Patricia Eldredge. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

## 21.1: Overview of Periodic Trends

### Problems

1. List three physical properties that are important in describing the behavior of the main group elements.
2. Arrange K, Cs, Sr, Ca, Ba, and Li in order of

    a. increasing ionization energy.
    b. increasing atomic size.
    c. increasing electronegativity.

3. Arrange Rb, H, Be, Na, Cs, and Ca in order of

    a. decreasing atomic size.
    b. decreasing magnitude of electron affinity.

4. Which periodic trends are affected by $Z_{eff}$? Based on the positions of the elements in the periodic table, which element would you expect to have the highest $Z_{eff}$? the lowest $Z_{eff}$?
5. Compare the properties of the metals and nonmetals with regard to their electronegativities and preferred oxidation states.
6. Of Ca, Br, Li, N, Zr, Ar, Sr, and S, which elements have a greater tendency to form positive ions than negative ions?
7. Arrange As, O, Ca, Sn, Be, and Sb in order of decreasing metallic character.
8. Give three reasons the chemistry of the second-period elements is generally not representative of their groups as a whole.
9. Compare the second-period elements and their heavier congeners with regard to

    a. magnitude of electron affinity.
    b. coordination number.
    c. the solubility of the halides in nonpolar solvents.

10. The heavier main group elements tend to form extended sigma-bonded structures rather than multiple bonds to other atoms. Give a reasonable explanation for this tendency.
11. What is the diagonal effect? How does it explain the similarity in chemistry between, for example, boron and silicon?
12. Although many of the properties of the second- and third-period elements in a group are quite different, one property is similar. Which one?
13. Two elements are effective additives to solid rocket propellant: beryllium and one other element that has similar chemistry. Based on the position of beryllium in the periodic table, identify the second element.

14. Give two reasons for the inert-pair effect. How would this phenomenon explain why $Sn^{2+}$ is a better reducing agent than $Pb^{2+}$?
15. Explain the following trend in electron affinities: Al (−41.8 kJ/mol), Si (−134.1 kJ/mol), P (−72.0 kJ/mol), and S (−200.4 kJ/mol).
16. Using orbital energy arguments, explain why electron configurations with more than four electron pairs around the central atom are not observed for second-period elements.

### Answers

3.
    a. Cs > Rb > Ca > Na > Be > H
    b. H > Na > Rb > Cs > Ca > Be
7. Ca > Be > Sn > Sb > As > O

13. aluminum

15. The magnitude of electron affinity increases from left to right in a period due to the increase in $Z_{eff}$; P has a lower electron affinity than expected due to its half-filled 3p shell, which requires the added electron to enter an already occupied 3p orbital.

### Structure and Reactivity

1. The following table lists the valences, coordination numbers, and ionic radii for a series of cations. Which would you substitute for $K^+$ in a crystalline lattice? Explain your answer.

| Metal | Charge | Coordination Number | Ionic Radius (pm) |
|---|---|---|---|
| Li | +1 | 4 | 76 |
| Na | +1 | 6 | 102 |
| K | +1 | 6 | 138 |
| Mg | +2 | 6 | 72 |
| Ca | +2 | 6 | 100 |
| Sr | +2 | 6 | 118 |

### Answer

1. $Sr^{2+}$; it is the ion with the radius closest to that of $K^+$.

## 21.2: The Chemistry of Hydrogen

## 21.3: The Alkali Metals (Group 1)

## 22.4: The Alkaline Earth Metals (Group 2)

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# CHAPTER OVERVIEW

## 21: The p-Block Elements


21.1: The Elements of Group 13
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# 21.1: The Elements of Group 13

**Learning Objectives**

- To understand the trends in properties and the reactivity of the group 13 elements.

Group 13 is the first group to span the dividing line between metals and nonmetals, so its chemistry is more diverse than that of groups 1 and 2, which include only metallic elements. Except for the lightest element (boron), the group 13 elements are all relatively electropositive; that is, they tend to lose electrons in chemical reactions rather than gain them. Although group 13 includes aluminum, the most abundant metal on Earth, none of these elements was known until the early 19th century because they are never found in nature in their free state. Elemental boron and aluminum, which were first prepared by reducing $B_2O_3$ and $AlCl_3$, respectively, with potassium, could not be prepared until potassium had been isolated and shown to be a potent reductant. Indium (In) and thallium (Tl) were discovered in the 1860s by using spectroscopic techniques, long before methods were available for isolating them. Indium, named for its indigo (deep blue-violet) emission line, was first observed in the spectrum of zinc ores, while thallium (from the Greek thallos, meaning "a young, green shoot of a plant") was named for its brilliant green emission line. Gallium (Ga; Mendeleev's eka-aluminum) was discovered in 1875 by the French chemist Paul Émile Lecoq de Boisbaudran during a systematic search for Mendeleev's "missing" element in group 13.

> *Group 13 elements are never found in nature in their free state.*

## Preparation and General Properties of the Group 13 Elements

As reductants, the group 13 elements are less powerful than the alkali metals and alkaline earth metals. Nevertheless, their compounds with oxygen are thermodynamically stable, and large amounts of energy are needed to isolate even the two most accessible elements—boron and aluminum—from their oxide ores.

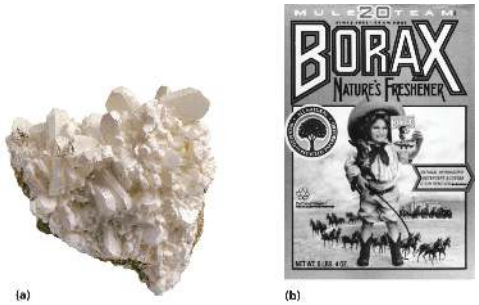



Figure 21.1.1: Borax Deposits. *(a) Concentrated deposits of crystalline borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds, such as the Mojave Desert and Death Valley in the western United States. (b) Borax is used in various cleaning products, including 20 Mule Team Borax, a laundry detergent named for the teams of 20 mules that hauled wagons full of borax from desert deposits to railroad terminals in the 1880s.*

Although boron is relatively rare (it is about 10,000 times less abundant than aluminum), concentrated deposits of borax [$Na_2B_4O_5(OH)_4{\cdot}8H_2O$] are found in ancient lake beds (Figure 21.1.1) and were used in ancient times for making glass and glazing pottery. Boron is produced on a large scale by reacting borax with acid to produce boric acid [$B(OH)_3$], which is then dehydrated to the oxide ($B_2O_3$). Reduction of the oxide with magnesium or sodium gives amorphous boron that is only about 95% pure:

$$Na_2B_4O_5(OH)_4 \cdot 8H_2O(s) \xrightarrow{\text{acid}} B(OH)_3(s) \xrightarrow{\Delta} B_2O_3(s) \tag{21.1.1}$$

$$B_2O_3(s) + 3Mg(s) \xrightarrow{\Delta} 2B(s) + 3MgO(s) \tag{21.1.2}$$

Pure, crystalline boron, however, is extremely difficult to obtain because of its high melting point (2300°C) and the highly corrosive nature of liquid boron. It is usually prepared by reducing pure $BCl_3$ with hydrogen gas at high temperatures or by the thermal decomposition of boron hydrides such as diborane ($B_2H_6$):

$$BCl_3(g) + \frac{3}{2}H_2(g) \rightarrow B(s) + 3HCl(g) \tag{21.1.3}$$

$$B_2H_{6(g)} \rightarrow 2B_{(s)} + 3H_{2(g)} \tag{21.1.4}$$

The reaction shown in Equation 21.1.3 is used to prepare boron fibers, which are stiff and light. Hence they are used as structural reinforcing materials in objects as diverse as the US space shuttle and the frames of lightweight bicycles that are used in races such as the Tour de France. Boron is also an important component of many ceramics and heat-resistant borosilicate glasses, such as Pyrex, which is used for ovenware and laboratory glassware.

In contrast to boron, deposits of aluminum ores such as bauxite, a hydrated form of $Al_2O_3$, are abundant. With an electrical conductivity about twice that of copper on a weight for weight basis, aluminum is used in more than 90% of the overhead electric power lines in the United States. However, because aluminum–oxygen compounds are stable, obtaining aluminum metal from bauxite is an expensive process. Aluminum is extracted from oxide ores by treatment with a strong base, which produces the soluble hydroxide complex $[Al(OH)_4]^-$. Neutralization of the resulting solution with gaseous $CO_2$ results in the precipitation of $Al(OH)_3$:

$$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} \tag{21.1.5}$$

Thermal dehydration of $Al(OH)_3$ produces $Al_2O_3$, and metallic aluminum is obtained by the electrolytic reduction of $Al_2O_3$ using the **Hall–Heroult process**. Of the group 13 elements, only aluminum is used on a large scale: for example, each Boeing 777 airplane is about 50% aluminum by mass.

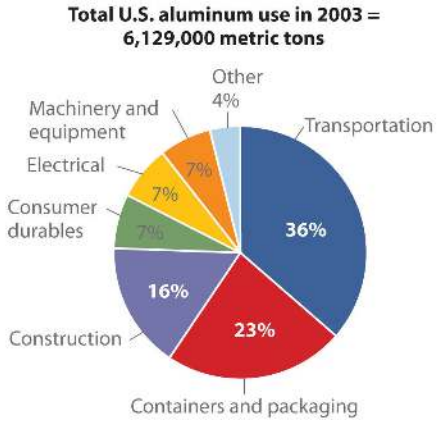



Figure 21.1.2: Source: Thomas D. Kelly and Grecia R. Matos, “Historical Statistics for Mineral and Material Commodities in the United States,” US Geological Survey Data Series 140, 2010, accessed July 20, 2011, pubs.usgs.gov/ds/2005/140/.

The other members of group 13 are rather rare: gallium is approximately 5000 times less abundant than aluminum, and indium and thallium are even scarcer. Consequently, these metals are usually obtained as by-products in the processing of other metals. The extremely low melting point of gallium (29.6°C), however, makes it easy to separate from aluminum. Due to its low melting point and high boiling point, gallium is used as a liquid in thermometers that have a temperature range of almost 2200°C. Indium and thallium, the heavier group 13 elements, are found as trace impurities in sulfide ores of zinc and lead. Indium is used as a crushable seal for high-vacuum cryogenic devices, and its alloys are used as low-melting solders in electronic circuit boards. Thallium, on the other hand, is so toxic that the metal and its compounds have few uses. Both indium and thallium oxides are released in flue dust when sulfide ores are converted to metal oxides and $SO_2$. Until relatively recently, these and other toxic elements were allowed to disperse in the air, creating large “dead zones” downwind of a smelter. The flue dusts are now trapped and serve as a relatively rich source of elements such as In and Tl (as well as Ge, Cd, Te, and As).

Table 21.1.1 summarizes some important properties of the group 13 elements. Notice the large differences between boron and aluminum in size, ionization energy, electronegativity, and standard reduction potential, which is consistent with the observation that boron behaves chemically like a nonmetal and aluminum like a metal. All group 13 elements have $ns^2np^1$ valence electron configurations, and all tend to lose their three valence electrons to form compounds in the +3 oxidation state. The heavier elements in the group can also form compounds in the +1 oxidation state formed by the formal loss of the single np valence electron. Because the group 13 elements generally contain only six valence electrons in their neutral compounds, these compounds are all moderately strong Lewis acids.

Table 21.1.1: Selected Properties of the Group 13 Elements

| Property | Boron | Aluminum* | Gallium | Indium | Thallium |
|---|---|---|---|---|---|
| atomic symbol | B | Al | Ga | In | Tl |
| atomic number | 5 | 13 | 31 | 49 | 81 |
| atomic mass (amu) | 10.81 | 26.98 | 69.72 | 114.82 | 204.38 |
| valence electron configuration† | $2s^2 2p^1$ | $3s^2 3p^1$ | $4s^2 4p^1$ | $5s^2 5p^1$ | $6s^2 6p^1$ |
| melting point/boiling point (°C) | 2075/4000 | 660/2519 | 29.7/2204 | 156.6/2072 | 304/1473 |
| density ($g/cm^3$) at 25°C | 2.34 | 2.70 | 5.91 | 7.31 | 11.8 |
| atomic radius (pm) | 87 | 118 | 136 | 156 | 156 |
| first ionization energy (kJ/mol) | 801 | 578 | 579 | 558 | 589 |
| most common oxidation state | +3 | +3 | +3 | +3 | +1 |
| ionic radius (pm)‡ | −25 | 54 | 62 | 80 | 162 |
| electron affinity (kJ/mol) | −27 | −42 | −40 | −39 | −37 |
| electronegativity | 2.0 | 1.6 | 1.8 | 1.8 | 1.8 |
| standard reduction potential (E°, V) | −0.87 | −1.66 | −0.55 | −0.34 | +0.741 of $M^{3+}(aq)$ |
| product of reaction with $O_2$ | $B_2O_3$ | $Al_2O_3$ | $Ga_2O_3$ | $In_2O_3$ | $Tl_2O$ |
| type of oxide | acidic | amphoteric | amphoteric | amphoteric | basic |
| product of reaction with $N_2$ | BN | AlN | GaN | InN | none |
| product of reaction with $X_2$§ | $BX_3$ | $Al_2X_6$ | $Ga_2X_6$ | $In_2X_6$ | TlX |

*This is the name used in the United States; the rest of the world inserts an extra i and calls it aluminium.

†The configuration shown does not include filled d and f subshells.

‡The values cited are for six-coordinate ions in the most common oxidation state, except for $Al^{3+}$, for which the value for the four-coordinate ion is given. The $B^{3+}$ ion is not a known species; the radius cited is an estimated four-coordinate value.

§X is Cl, Br, or I. Reaction with $F_2$ gives the trifluorides ($MF_3$) for all group 13 elements.

> *Neutral compounds of the group 13 elements are electron deficient, so they are generally moderately strong Lewis acids.*

In contrast to groups 1 and 2, the group 13 elements show no consistent trends in ionization energies, electron affinities, and reduction potentials, whereas electronegativities actually increase from aluminum to thallium. Some of these anomalies, especially

for the series Ga, In, Tl, can be explained by the increase in the effective nuclear charge ($Z_{eff}$) that results from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Consequently, although the actual nuclear charge increases by 32 as we go from indium to thallium, screening by the filled 5d and 4f subshells is so poor that $Z_{eff}$ increases significantly from indium to thallium. Thus the first ionization energy of thallium is actually greater than that of indium.

> *Anomalies in periodic trends among Ga, In, and Tl can be explained by the increase in the effective nuclear charge due to poor shielding.*

## Reactions and Compounds of Boron

Elemental boron is a semimetal that is remarkably unreactive; in contrast, the other group 13 elements all exhibit metallic properties and reactivity. We therefore consider the reactions and compounds of boron separately from those of other elements in the group. All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalized, metallic bonding. With its high ionization energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalized valence electrons. Instead, boron forms unique and intricate structures that contain multicenter bonds, in which a pair of electrons holds together three or more atoms.

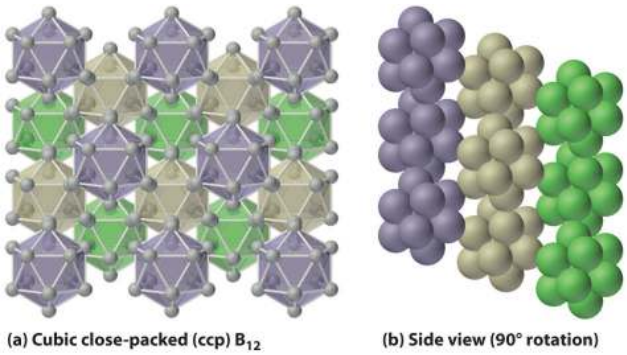



Figure 21.1.3: Solid Boron Contains $B_{12}$ Icosahedra. Unlike metallic solids, elemental boron consists of a regular array of $B_{12}$ icosahedra rather than individual boron atoms. Note that each boron atom in the $B_{12}$ icosahedron is connected to five other boron atoms within the $B_{12}$ unit. (a) The allotrope of boron with the simplest structure is α-rhombohedral boron, which consists of $B_{12}$ octahedra in an almost cubic close-packed lattice. (b) A side view of the structure shows that icosahedra do not pack as efficiently as spheres, making the density of solid boron less than expected.

> *Elemental boron forms multicenter bonds, whereas the other group 13 elements exhibit metallic bonding.*

The basic building block of elemental boron is not the individual boron atom, as would be the case in a metal, but rather the $B_{12}$ icosahedron. Because these icosahedra do not pack together very well, the structure of solid boron contains voids, resulting in its low density (Figure 21.1.3). Elemental boron can be induced to react with many nonmetallic elements to give binary compounds that have a variety of applications. For example, plates of boron carbide ($B_4C$) can stop a 30-caliber, armor-piercing bullet, yet they weigh 10%–30% less than conventional armor. Other important compounds of boron with nonmetals include boron nitride (BN), which is produced by heating boron with excess nitrogen (Equation 21.1.6); boron oxide ($B_2O_3$), which is formed when boron is heated with excess oxygen (Equation 21.1.7); and the boron trihalides ($BX_3$), which are formed by heating boron with excess halogen (Equation 21.1.8).

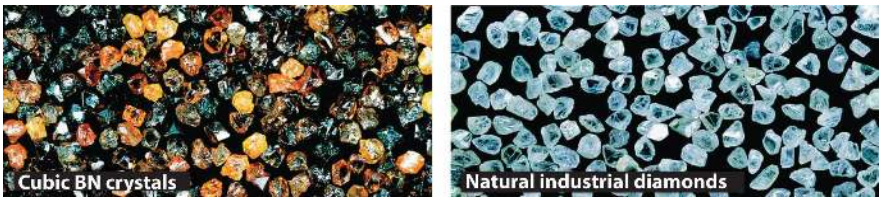
$$2B(s) + N_2(g) \xrightarrow{\Delta} 2BN(s) \tag{21.1.6}$$

$$4B(s) + 3O_2(g) \xrightarrow{\Delta} 2B_2O_3(s) \tag{21.1.7}$$

$$2B(s) + 3X_2(g) \xrightarrow{\Delta} 2BX_3(g) \tag{21.1.8}$$

As is typical of elements lying near the dividing line between metals and nonmetals, many compounds of boron are amphoteric, dissolving in either acid or base.

Boron nitride is similar in many ways to elemental carbon. With eight electrons, the B–N unit is isoelectronic with the C–C unit, and B and N have the same average size and electronegativity as C. The most stable form of BN is similar to graphite, containing six-membered $B_3N_3$ rings arranged in layers. At high temperature and pressure, hexagonal BN converts to a cubic structure similar to diamond, which is one of the hardest substances known. Boron oxide ($B_2O_3$) contains layers of trigonal planar $BO_3$ groups (analogous to $BX_3$) in which the oxygen atoms bridge two boron atoms. It dissolves many metal and nonmetal oxides, including $SiO_2$, to give a wide range of commercially important borosilicate glasses. A small amount of CoO gives the deep blue color characteristic of “cobalt blue” glass.




At high temperatures, boron also reacts with virtually all metals to give metal borides that contain regular three-dimensional networks, or clusters, of boron atoms. The structures of two metal borides—$ScB_{12}$ and $CaB_6$—are shown in Figure 21.1.4. Because metal-rich borides such as $ZrB_2$ and $TiB_2$ are hard and corrosion resistant even at high temperatures, they are used in applications such as turbine blades and rocket nozzles.

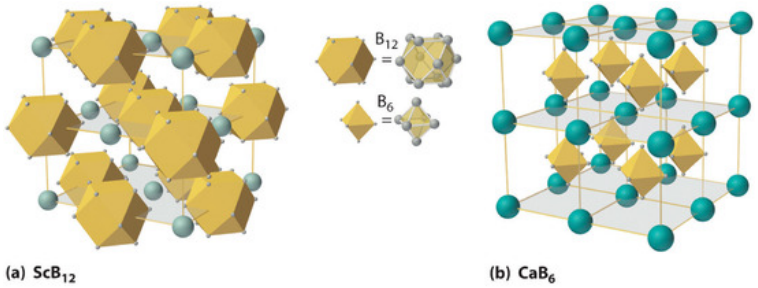



Figure 21.1.4: The Structures of $ScB_{12}$and $CaB_6$, Two Boron-Rich Metal Borides. *(a) The structure of $ScB_{12}$ consists of $B_{12}$ clusters and Sc atoms arranged in a faced-centered cubic lattice similar to that of NaCl, with $B_{12}$units occupying the anion positions and scandium atoms the cation positions. The B12 units here are not icosahedra but cubooctahedra, with alternating square and triangular faces. (b) The structure of $CaB_6$ consists of octahedral $B_6$ clusters and calcium atoms arranged in a body-centered cubic lattice similar to that of CsCl, with $B_6$ units occupying the anion positions and calcium atoms the cation positions.*

Boron hydrides were not discovered until the early 20th century, when the German chemist Alfred Stock undertook a systematic investigation of the binary compounds of boron and hydrogen, although binary hydrides of carbon, nitrogen, oxygen, and fluorine have been known since the 18th century. Between 1912 and 1936, Stock oversaw the preparation of a series of boron–hydrogen compounds with unprecedented structures that could not be explained with simple bonding theories. All these compounds contain multicenter bonds. The simplest example is diborane ($B_2H_6$), which contains two bridging hydrogen atoms (part (a) in Figure 21.1.5. An extraordinary variety of polyhedral boron–hydrogen clusters is now known; one example is the $B_{12}H_{12}^{2-}$ ion, which has a polyhedral structure similar to the icosahedral $B_{12}$ unit of elemental boron, with a single hydrogen atom bonded to each boron atom.

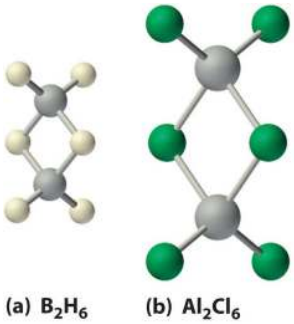
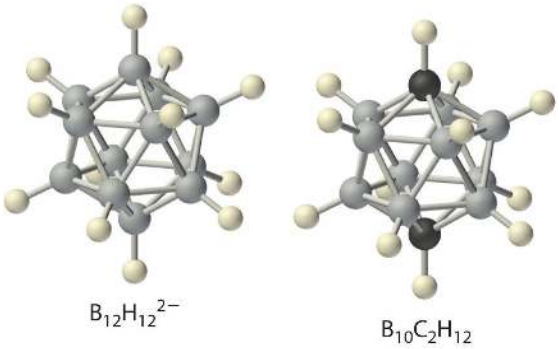



Figure 21.1.5: The Structures of Diborane ($B_2H_6$) and Aluminum Chloride ($Al_2Cl_6$). (a) The hydrogen-bridged dimer $B_2H_6$ contains two three-center, two-electron bonds as described for the $B_2H_7^-$ ion in Figure 21.5. (b) In contrast, the bonding in the halogen-bridged dimer $Al_2Cl_6$ can be described in terms of electron-pair bonds, in which a chlorine atom bonded to one aluminum atom acts as a Lewis base by donating a lone pair of electrons to another aluminum atom, which acts as a Lewis acid.

A related class of polyhedral clusters, the carboranes, contain both CH and BH units; an example is shown here. Replacing the hydrogen atoms bonded to carbon with organic groups produces substances with novel properties, some of which are currently being investigated for their use as liquid crystals and in cancer chemotherapy.




The enthalpy of combustion of diborane ($B_2H_6$) is −2165 kJ/mol, one of the highest values known:

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O(l) \qquad \Delta H_{comb} = -2165\ kJ/mol \tag{21.1.9}$$

Consequently, the US military explored using boron hydrides as rocket fuels in the 1950s and 1960s. This effort was eventually abandoned because boron hydrides are unstable, costly, and toxic, and, most important, $B_2O_3$ proved to be highly abrasive to rocket nozzles. Reactions carried out during this investigation, however, showed that boron hydrides exhibit unusual reactivity.

Because boron and hydrogen have almost identical electronegativities, the reactions of boron hydrides are dictated by minor differences in the distribution of electron density in a given compound. In general, two distinct types of reaction are observed: electron-rich species such as the $BH_4^-$ ion are reductants, whereas electron-deficient species such as $B_2H_6$ act as oxidants.

### Example 21.1.1

For each reaction, explain why the given products form.

a. $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$
b. $BCl_3(l) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3HCl(aq)$
c. $2BI_3(s) + 3H_2(g) \xrightarrow{\Delta} \frac{1}{6}B_{12}(s) + 6HI(g)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

**Solution**

a. Molecular oxygen is an oxidant. If the other reactant is a potential reductant, we expect that a redox reaction will occur. Although $B_2H_6$ contains boron in its highest oxidation state (+3), it also contains hydrogen in the −1 oxidation state (the hydride ion). Because hydride is a strong reductant, a redox reaction will probably occur. We expect that $H^-$ will be oxidized to $H^+$ and $O_2$ will be reduced to $O^{2-}$, but what are the actual products? A reasonable guess is $B_2O_3$ and $H_2O$, both stable compounds.

b. Neither $BCl_3$ nor water is a powerful oxidant or reductant, so a redox reaction is unlikely; a hydrolysis reaction is more probable. Nonmetal halides are acidic and react with water to form a solution of the hydrohalic acid and a nonmetal oxide or hydroxide. In this case, the most probable boron-containing product is boric acid [$B(OH)_3$].

c. We normally expect a boron trihalide to behave like a Lewis acid. In this case, however, the other reactant is elemental hydrogen, which usually acts as a reductant. The iodine atoms in $BI_3$ are in the lowest accessible oxidation state (−1), and boron is in the +3 oxidation state. Consequently, we can write a redox reaction in which hydrogen is oxidized and boron is reduced. Because compounds of boron in lower oxidation states are rare, we expect that boron will be reduced to elemental boron. The other product of the reaction must therefore be HI.

**? Exercise 21.1.1**

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $B_2H_6(g) + H_2O(l) \xrightarrow{\Delta}$

b. $BBr_3(l) + O_2(g) \rightarrow$

c. $B_2O_3(s) + Ca(s) \xrightarrow{\Delta}$

**Answer**

a. $B_2H_6(g) + H_2O(l) \xrightarrow{\Delta} 2B(OH)_3(s) + 6H_2(g)$

b. $BBr_3(l) + O_2(g) \rightarrow$ no reaction

c. $6B_2O_3(s) + 18Ca(s) \xrightarrow{\Delta} B_{12}(s) + 18CaO(s)$

## Reactions and Compounds of the Heavier Group 13 Elements

All four of the heavier group 13 elements (Al, Ga, In, and Tl) react readily with the halogens to form compounds with a 1:3 stoichiometry:

$$2M_{(s)} + 3X_{2(s,l,g)} \rightarrow 2MX_{3(s)} \text{ or } M_2X_6 \tag{21.1.10}$$

The reaction of Tl with iodine is an exception: although the product has the stoichiometry $TlI_3$, it is not thallium(III) iodide, but rather a thallium(I) compound, the $Tl^+$ salt of the triiodide ion ($I_3^-$). This compound forms because iodine is not a powerful enough oxidant to oxidize thallium to the +3 oxidation state.

Of the halides, only the fluorides exhibit behavior typical of an ionic compound: they have high melting points (>950°C) and low solubility in nonpolar solvents. In contrast, the trichorides, tribromides, and triiodides of aluminum, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers (part (b) in Figure 21.1.4). Although the structure of these dimers is similar to that of diborane ($B_2H_6$), the bonding can be described in terms of electron-pair bonds rather than the delocalized electron-deficient bonding found in diborane. Bridging halides are poor electron-pair donors, so the group 13 trihalides are potent Lewis acids that react readily with Lewis bases, such as amines, to form a Lewis acid–base adduct:

$$Al_2Cl_{6(soln)} + 2(CH_3)_3N_{(soln)} \rightarrow 2(CH_3)_3N : AlCl_{3(soln)} \tag{21.1.11}$$

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide (\[M(OH)_3\)):

$$MX_{3(s)} + 3H_2O_{(l)} \rightarrow M(OH)_{3(s)} + 3HX_{(aq)} \tag{21.1.12}$$

In a related reaction, $Al_2(SO_4)_3$ is used to clarify drinking water by the precipitation of hydrated $Al(OH)_3$, which traps particulates. The halides of the heavier metals (In and Tl) are less reactive with water because of their lower charge-to-radius ratio. Instead of forming hydroxides, they dissolve to form the hydrated metal complex ions: $[M(H_2O)_6]^{3+}$.

> *Of the group 13 halides, only the fluorides behave as typical ionic compounds.*

Like boron (Equation 21.1.7), all the heavier group 13 elements react with excess oxygen at elevated temperatures to give the trivalent oxide ($M_2O_3$), although $Tl_2O_3$ is unstable:

$$4M(s) + 3O_2(g) \xrightarrow{\Delta} 2M_2O_3(s) \tag{21.1.13}$$

Aluminum oxide ($Al_2O_3$), also known as alumina, is a hard, high-melting-point, chemically inert insulator used as a ceramic and as an abrasive in sandpaper and toothpaste. Replacing a small number of $Al^{3+}$ ions in crystalline alumina with $Cr^{3+}$ ions forms the gemstone ruby, whereas replacing $Al^{3+}$ with a mixture of $Fe^{2+}$, $Fe^{3+}$, and $Ti^{4+}$ produces blue sapphires. The gallium oxide compound $MgGa_2O_4$ gives the brilliant green light familiar to anyone who has ever operated a xerographic copy machine. All the oxides dissolve in dilute acid, but $Al_2O_3$ and $Ga_2O_3$ are amphoteric, which is consistent with their location along the diagonal line of the periodic table, also dissolving in concentrated aqueous base to form solutions that contain $M(OH)_4^-$ ions.

> *Group 13 trihalides are potent Lewis acids that react with Lewis bases to form a Lewis acid–base adduct.*

Aluminum, gallium, and indium also react with the other group 16 elements (chalcogens) to form chalcogenides with the stoichiometry $M_2Y_3$. However, because Tl(III) is too strong an oxidant to form a stable compound with electron-rich anions such as $S^{2-}$, $Se^{2-}$, and $Te^{2-}$, thallium forms only the thallium(I) chalcogenides with the stoichiometry $Tl_2Y$. Only aluminum, like boron, reacts directly with $N_2$ (at very high temperatures) to give AlN, which is used in transistors and microwave devices as a nontoxic heat sink because of its thermal stability; GaN and InN can be prepared using other methods. All the metals, again except Tl, also react with the heavier group 15 elements (pnicogens) to form the so-called III–V compounds, such as GaAs. These are semiconductors, whose electronic properties, such as their band gaps, differ from those that can be achieved using either pure or doped group 14 elements. For example, nitrogen- and phosphorus-doped gallium arsenide ($GaAs_{1-x-y}P_xN_y$) is used in the displays of calculators and digital watches.

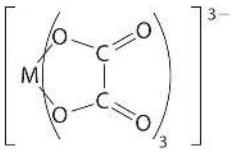
> *All group 13 oxides dissolve in dilute acid, but $Al_2O_3$ and $Ga_2O_3$ are amphoteric.*

Unlike boron, the heavier group 13 elements do not react directly with hydrogen. Only the aluminum and gallium hydrides are known, but they must be prepared indirectly; $AlH_3$ is an insoluble, polymeric solid that is rapidly decomposed by water, whereas $GaH_3$ is unstable at room temperature.

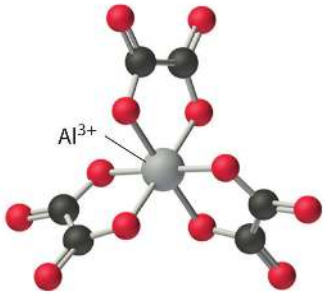
## Complexes of Group 13 Elements

Boron has a relatively limited tendency to form complexes, but aluminum, gallium, indium, and, to some extent, thallium form many complexes. Some of the simplest are the hydrated metal ions $[M(H_2O)_6^{3+}]$, which are relatively strong Brønsted–Lowry acids that can lose a proton to form the $M(H_2O)_5(OH)^{2+}$ ion:

$$[M(H_2O)_6]^{3+}_{(aq)} \rightarrow M(H_2O)_5(OH)^{2+}_{(aq)} + H^+_{(aq)} \tag{21.1.14}$$




Oxalate ion




$Al^{3+}$–oxalate complex

Group 13 metal ions also form stable complexes with species that contain two or more negatively charged groups, such as the oxalate ion. The stability of such complexes increases as the number of coordinating groups provided by the ligand increases.

## Example 21.1.2

For each reaction, explain why the given products form.

a. $2Al(s) + Fe_2O_3(s) \xrightarrow{\Delta} 2Fe(l) + Al_2O_3(s)$
b. $2Ga(s) + 6H_2O(l) + 2OH^-(aq) \xrightarrow{\Delta} 3H_2(g) + 2Ga(OH)_4^-(aq)$
c. $In_2Cl_6(s) \xrightarrow{H_2O(l)} 2In^{3+}(aq) + 6Cl^-(aq)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

**Solution**

a. Aluminum is an active metal and a powerful reductant, and $Fe_2O_3$ contains Fe(III), a potential oxidant. Hence a redox reaction is probable, producing metallic Fe and $Al_2O_3$. Because Al is a main group element that lies above Fe, which is a transition element, it should be a more active metal than Fe. Thus the reaction should proceed to the right. In fact, this is the thermite reaction, which is so vigorous that it produces molten Fe and can be used for welding.
b. Gallium lies immediately below aluminum in the periodic table and is amphoteric, so it will dissolve in either acid or base to produce hydrogen gas. Because gallium is similar to aluminum in many of its properties, we predict that gallium will dissolve in the strong base.
c. The metallic character of the group 13 elements increases with increasing atomic number. Indium trichloride should therefore behave like a typical metal halide, dissolving in water to form the hydrated cation.

## Exercise 21.1.2

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $LiH(s) + Al_2Cl_6(soln) \rightarrow$
b. $Al_2O_3(s) + OH^-(aq) \rightarrow$
c. $Al(s) + N_2(g) \xrightarrow{\Delta}$

d. $Ga_2Cl_6(soln) + Cl^-(soln) \rightarrow$

**Answer**

a. $8LiH(s) + Al_2Cl_6(soln) \rightarrow 2LiAlH_4(soln) + 6LiCl(s)$
b. $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$
c. $2Al(s) + N_2(g) \xrightarrow{\Delta} 2AlN(s)$
d. $Ga_2Cl_6(soln) + 2Cl^-(soln) \rightarrow 2GaCl_4^-(soln)$

## Summary

Compounds of the group 13 elements with oxygen are thermodynamically stable. Many of the anomalous properties of the group 13 elements can be explained by the increase in $Z_{eff}$ moving down the group. Isolation of the group 13 elements requires a large amount of energy because compounds of the group 13 elements with oxygen are thermodynamically stable. Boron behaves chemically like a nonmetal, whereas its heavier congeners exhibit metallic behavior. Many of the inconsistencies observed in the properties of the group 13 elements can be explained by the increase in $Z_{eff}$ that arises from poor shielding of the nuclear charge by the filled $(n - 1)d^{10}$ and $(n - 2)f^{14}$ subshells. Instead of forming a metallic lattice with delocalized valence electrons, boron forms unique aggregates that contain multicenter bonds, including metal borides, in which boron is bonded to other boron atoms to form three-dimensional networks or clusters with regular geometric structures. All neutral compounds of the group 13 elements are electron deficient and behave like Lewis acids. The trivalent halides of the heavier elements form halogen-bridged dimers that contain electron-pair bonds, rather than the delocalized electron-deficient bonds characteristic of diborane. Their oxides dissolve in dilute acid, although the oxides of aluminum and gallium are amphoteric. None of the group 13 elements reacts directly with hydrogen, and the stability of the hydrides prepared by other routes decreases as we go down the group. In contrast to boron, the heavier group 13 elements form a large number of complexes in the +3 oxidation state.

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# 21.2: The Elements of Group 14

**Learning Objectives**

- To understand the trends in properties and reactivity of the group 14 elements.

The elements of group 14 show a greater range of chemical behavior than any other family in the periodic table. Three of the five elements—carbon, tin, and lead—have been known since ancient times. For example, some of the oldest known writings are Egyptian hieroglyphics written on papyrus with ink made from lampblack, a finely divided carbon soot produced by the incomplete combustion of hydrocarbons (Figure 21.2.1). Activated carbon is an even more finely divided form of carbon that is produced from the thermal decomposition of organic materials, such as sawdust. Because it adsorbs many organic and sulfur-containing compounds, activated carbon is used to decolorize foods, such as sugar, and to purify gases and wastewater.

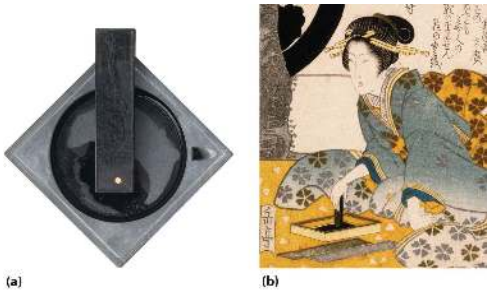



Figure 21.2.1: Very Small Particles of Noncrystalline Carbon Are Used to Make Black Ink. *(a) Since ancient times, ink sticks have been the major source of black ink in Asia. Plant oils or resinous woods such as pine are burned, and the resulting soot (lampblack) is collected, mixed with binders such as animal glues and minerals, compressed into a solid stick, and allowed to dry. Liquid ink is made by rubbing the ink stick against the surface of a special stone ink dish with small amounts of water. (b) A 19th-century Japanese painting illustrates how ink is made from an ink stick.*

Tin and lead oxides and sulfides are easily reduced to the metal by heating with charcoal, a discovery that must have occurred by accident when prehistoric humans used rocks containing their ores for a cooking fire. However, because tin and copper ores are often found together in nature, their alloy—bronze—was probably discovered before either element, a discovery that led to the Bronze Age. The heaviest element in group 14, lead, is such a soft and malleable metal that the ancient Romans used thin lead foils as writing tablets, as well as lead cookware and lead pipes for plumbing. (Recall that the atomic symbols for tin and lead come from their Latin names: Sn for stannum and Pb for plumbum.)

Although the first glasses were prepared from silica (silicon oxide, $SiO_2$) around 1500 BC, elemental silicon was not prepared until 1824 because of its high affinity for oxygen. Jöns Jakob Berzelius was finally able to obtain amorphous silicon by reducing $Na_2SiF_6$ with molten potassium. The crystalline element, which has a shiny blue-gray luster, was not isolated until 30 yr later. The last member of the group 14 elements to be discovered was germanium, which was found in 1886 in a newly discovered silver-colored ore by the German chemist Clemens Winkler, who named the element in honor of his native country.

## Preparation and General Properties of the Group 14 Elements

The natural abundance of the group 14 elements varies tremendously. Elemental carbon, for example, ranks only 17th on the list of constituents of Earth's crust. Pure graphite is obtained by reacting coke, an amorphous form of carbon used as a reductant in the production of steel, with silica to give silicon carbide (SiC). This is then thermally decomposed at very high temperatures (2700°C) to give graphite:

$$SiO_2(s) + 3C(s) \xrightarrow{\Delta} SiC(s) + 2CO(g) \tag{21.2.1}$$

$$SiC(s) \xrightarrow{\Delta} Si(s) + C(\text{graphite}) \tag{21.2.2}$$

One allotrope of carbon, diamond, is metastable under normal conditions, with a $\Delta G°_f$ of 2.9 kJ/mol versus graphite. At pressures greater than 50,000 atm, however, the diamond structure is favored and is the most stable form of carbon. Because the structure of diamond is more compact than that of graphite, its density is significantly higher (3.51 g/cm$^3$ versus 2.2 g/cm$^3$). Because of its high thermal conductivity, diamond powder is used to transfer heat in electronic devices.

The most common sources of diamonds on Earth are ancient volcanic pipes that contain a rock called kimberlite, a lava that solidified rapidly from deep inside the Earth. Most kimberlite formations, however, are much newer than the diamonds they contain. In fact, the relative amounts of different carbon isotopes in diamond show that diamond is a chemical and geological "fossil" older than our solar system, which means that diamonds on Earth predate the existence of our sun. Thus diamonds were most likely created deep inside Earth from primordial grains of graphite present when Earth was formed (part (a) in Figure 21.2.2). Gem-quality diamonds can now be produced synthetically and have chemical, optical, and physical characteristics identical to those of the highest-grade natural diamonds.

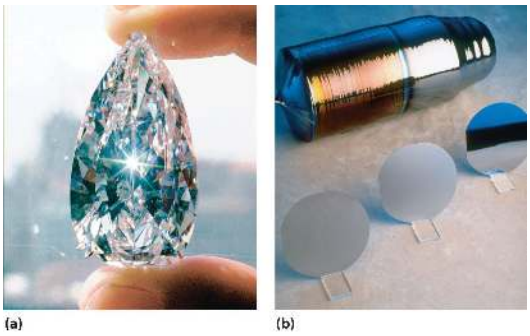



Figure 21.2.2: Crystalline Samples of Carbon and Silicon, the Lightest Group 14 Elements. (a) The 78.86-carat Ahmadabad diamond, a historic Indian gem purchased in Gujarat in the 17th century by the French explorer Jean-Baptiste Tavernier and sold in 1995 for $4.3 million, is a rare example of a large single crystal of diamond, the less-stable allotrope of carbon. (b) Large single crystals of highly purified silicon are the basis of the modern electronics industry. They are sliced into very thin wafers that are highly polished and then cut into smaller pieces for use as chips.

Although oxygen is the most abundant element on Earth, the next most abundant is silicon, the next member of group 14. Pure silicon is obtained by reacting impure silicon with $Cl_2$ to give $SiCl_4$, followed by the fractional distillation of the impure $SiCl_4$ and reduction with $H_2$:

$$SiCl_4(l) + 2H_2(g) \xrightarrow{\Delta} Si(s) + 4HCl(g) \tag{21.2.3}$$

Several million tons of silicon are annually produced with this method. Amorphous silicon containing residual amounts of hydrogen is used in photovoltaic devices that convert light to electricity, and silicon-based solar cells are used to power pocket calculators, boats, and highway signs, where access to electricity by conventional methods is difficult or expensive. Ultrapure silicon and germanium form the basis of the modern electronics industry (part (b) in Figure 21.2.2).

In contrast to silicon, the concentrations of germanium and tin in Earth's crust are only 1–2 ppm. The concentration of lead, which is the end product of the nuclear decay of many radionuclides, is 13 ppm, making lead by far the most abundant of the heavy group 14 elements. No concentrated ores of germanium are known; like indium, germanium is generally recovered from flue dusts obtained by processing the ores of metals such as zinc. Because germanium is essentially transparent to infrared radiation, it is used in optical devices.

Tin and lead are soft metals that are too weak for structural applications, but because tin is flexible, corrosion resistant, and nontoxic, it is used as a coating in food packaging. A "tin can," for example, is actually a steel can whose interior is coated with a thin layer (1–2 μm) of metallic tin. Tin is also used in superconducting magnets and low-melting-point alloys such as solder and pewter. Pure lead is obtained by heating galena (PbS) in air and reducing the oxide (PbO) to the metal with carbon, followed by electrolytic deposition to increase the purity:

$$PbS(s) + \frac{3}{2}O_2(g) \xrightarrow{\Delta} PbO(s) + SO_2(g) \tag{21.2.4}$$

$$PbO(s) + C(s) \xrightarrow{\Delta} Pb(l) + CO(g) \tag{21.2.5}$$

or

$$PbO(s) + CO(g) \xrightarrow{\Delta} Pb(l) + CO_2(g) \tag{21.2.6}$$

By far the single largest use of lead is in lead storage batteries. The group 14 elements all have $ns^2np^2$ valence electron configurations. All form compounds in which they formally lose either the two np and the two ns valence electrons or just the two np valence electrons, giving a +4 or +2 oxidation state, respectively. Because covalent bonds decrease in strength with increasing atomic size and the ionization energies for the heavier elements of the group are higher than expected due to a higher $Z_{eff}$, the relative stability of the +2 oxidation state increases smoothly from carbon to lead.

> *The relative stability of the +2 oxidation state increases, and the tendency to form catenated compounds decreases, from carbon to lead in group 14.*

Recall that many carbon compounds contain multiple bonds formed by π overlap of singly occupied 2p orbitals on adjacent atoms. Compounds of silicon, germanium, tin, and lead with the same stoichiometry as those of carbon, however, tend to have different structures and properties. For example, $CO_2$ is a gas that contains discrete O=C=O molecules, whereas the most common form of $SiO_2$ is the high-melting solid known as quartz, the major component of sand. Instead of discrete $SiO_2$ molecules, quartz contains a three-dimensional network of silicon atoms that is similar to the structure of diamond but with an oxygen atom inserted between each pair of silicon atoms. Thus each silicon atom is linked to four other silicon atoms by bridging oxygen atoms.

The tendency to catenate—to form chains of like atoms—decreases rapidly as we go down group 14 because bond energies for both the E–E and E–H bonds decrease with increasing atomic number (where E is any group 14 element). Consequently, inserting a $CH_2$ group into a linear hydrocarbon such as n-hexane is exergonic ($\Delta G° = -45$ kJ/mol), whereas inserting an $SiH_2$ group into the silicon analogue of n-hexane ($Si_6H_{14}$) actually costs energy ($\Delta G° \approx +25$ kJ/mol). As a result of this trend, the thermal stability of catenated compounds decreases rapidly from carbon to lead.

In Table 21.2.1 "Selected Properties of the Group 14 Elements" we see, once again, that there is a large difference between the lightest element (C) and the others in size, ionization energy, and electronegativity. As in group 13, the second and third elements (Si and Ge) are similar, and there is a reversal in the trends for some properties, such as ionization energy, between the fourth and fifth elements (Sn and Pb). As for group 13, these effects can be explained by the presence of filled (n − 1)d and (n − 2)f subshells, whose electrons are relatively poor at screening the outermost electrons from the higher nuclear charge.

Table 21.2.1: Selected Properties of the Group 14 Elements

| Property | Carbon | Silicon | Germanium | Tin | Lead |
|---|---|---|---|---|---|
| atomic symbol | C | Si | Ge | Sn | Pb |
| atomic number | 6 | 14 | 32 | 50 | 82 |
| atomic mass (amu) | 12.01 | 28.09 | 72.64 | 118.71 | 207.2 |
| valence electron configuration* | $2s^2 2p^2$ | $3s^2 3p^2$ | $4s^2 4p^2$ | $5s^2 5p^2$ | $6s^2 6p^2$ |
| melting point/boiling point (°C) | 4489 (at 10.3 MPa)/3825 | 1414/3265 | 939/2833 | 232/2602 | 327/1749 |
| density ($g/cm^3$) at 25°C | 2.2 (graphite), 3.51 (diamond) | 2.33 | 5.32 | 7.27(white) | 11.30 |
| atomic radius (pm) | 77 (diamond) | 111 | 125 | 145 | 154 |
| first ionization energy (kJ/mol) | 1087 | 787 | 762 | 709 | 716 |
| most common oxidation state | +4 | +4 | +4 | +4 | +4 |
| ionic radius (pm)† | ≈29 | ≈40 | 53 | 69 | 77.5 |
| electron affinity (kJ/mol) | −122 | −134 | −119 | −107 | −35 |
| electronegativity | 2.6 | 1.9 | 2.0 | 2.0 | 1.8 |
| standard reduction potential (E°, V) (for $EO_2 \rightarrow E$ in acidic solution) | 0.21 | −0.86 | −0.18 | −0.12 | 0.79 |
| product of reaction with $O_2$ | $CO_2$, CO | $SiO_2$ | $GeO_2$ | $SnO_2$ | PbO |
| type of oxide | acidic ($CO_2$) | acidic neutral (CO) | amphoteric | amphoteric | amphoteric |
| product of reaction with $N_2$ | none | $Si_3N_4$ | none | $Sn_3N_4$ | none |
| product of reaction with $X_2$‡ | $CX_4$ | $SiX_4$ | $GeX_4$ | $SnX_4$ | $PbX_2$ |
| product of reaction with $H_2$ | $CH_4$ | none | none | none | none |

*The configuration shown does not include filled d and f subshells.

†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for $C^{4+}$ and $Si^{4+}$, for which values for the four-coordinate ion are estimated.

‡X is Cl, Br, or I. Reaction with $F_2$ gives the tetrafluorides ($EF_4$) for all group 14 elements, where E represents any group 14 element.

The group 14 elements follow the same pattern as the group 13 elements in their periodic properties.

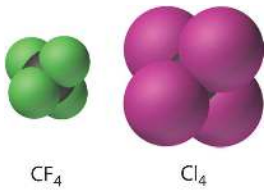
## Reactions and Compounds of Carbon

Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon—diamond, graphite, fullerenes, and nanotubes—are distinct, but they all contain simple electron-pair bonds (Figure 7.18). Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(–C{\equiv}C–C{\equiv}C–)_n$. Carbon nanotubes ("buckytubes") are being studied as potential building blocks for ultramicroscale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers.

Although all the carbon tetrahalides ($CX_4$) are known, they are generally not obtained by the direct reaction of carbon with the elemental halogens ($X_2$) but by indirect methods such as the following reaction, where X is Cl or Br:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \tag{21.2.7}$$




The carbon tetrahalides all have the tetrahedral geometry predicted by the valence-shell electron-pair repulsion (VSEPR) model, as shown for $CCl_4$ and $CI_4$. Their stability decreases rapidly as the halogen increases in size because of poor orbital overlap and increased crowding. Because the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C{=}CF_2$), analogous to polyethylene, is the nonstick Teflon lining found on many cooking pans, and similar compounds are used to make fabrics stain resistant (such as Scotch-Gard) or waterproof but breathable (such as Gore-Tex).

> *The stability of the carbon tetrahalides decreases with increasing size of the halogen due to increasingly poor orbital overlap and crowding.*

Carbon reacts with oxygen to form either CO or $CO_2$, depending on the stoichiometry. Carbon monoxide is a colorless, odorless, and poisonous gas that reacts with the iron in hemoglobin to form an Fe–CO unit, which prevents hemoglobin from binding, transporting, and releasing oxygen in the blood (see Figure 23.26). In the laboratory, carbon monoxide can be prepared on a small scale by dehydrating formic acid with concentrated sulfuric acid:

$$\mathrm{HCO_2H(l)} \xrightarrow{\mathrm{H_2SO_4(l)}} \mathrm{CO(g) + H_3O^+(aq) + HSO_4^-} \tag{21.2.8}$$

Carbon monoxide also reacts with the halogens to form the oxohalides ($COX_2$). Probably the best known of these is phosgene ($Cl_2C{=}O$), which is highly poisonous and was used as a chemical weapon during World War I:

$$\mathrm{CO(g) + Cl_2(g)} \xrightarrow{\Delta} \mathrm{Cl_2C{=}O(g)} \tag{21.2.9}$$

Despite its toxicity, phosgene is an important industrial chemical that is prepared on a large scale, primarily in the manufacture of polyurethanes.

Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, $CO_2$ reacts with water to form acidic solutions containing carbonic acid ($H_2CO_3$). In contrast to its reactions with oxygen, reacting carbon with sulfur at high temperatures produces only carbon disulfide ($CS_2$):

$$\mathrm{C(s) + 2S(g)} \xrightarrow{\Delta} \mathrm{CS_2(g)} \tag{21.2.10}$$

The selenium analog $CSe_2$ is also known. Both have the linear structure predicted by the VSEPR model, and both are vile smelling (and in the case of $CSe_2$, highly toxic), volatile liquids. The sulfur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C≡Y bonds (Y is S or Se) are much weaker than the C≡O bond due to poorer π orbital overlap.

> *π bonds between carbon and the heavier chalcogenides are weak due to poor orbital overlap.*

Binary compounds of carbon with less electronegative elements are called carbides. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high temperatures with electropositive metals such as those of groups 1 and 2 and aluminum produces ionic carbides, which contain discrete metal cations and carbon anions. The identity of the anions depends on the size of the second element. For example, smaller elements such as beryllium and aluminum give methides such as $Be_2C$ and $Al_4C_3$, which formally contain the $C^{4-}$ ion derived from methane ($CH_4$) by losing all four H atoms as protons. In contrast, larger metals such as sodium and calcium give carbides with stoichiometries of $Na_2C_2$ and $CaC_2$. Because these carbides contain the $C^{4-}$ ion, which is derived from acetylene (HC≡CH) by losing both H atoms as protons, they are more properly called acetylides. Reacting ionic carbides with dilute aqueous acid results in protonation of the anions to give the parent hydrocarbons: $CH_4$ or $C_2H_2$. For many years, miners' lamps used the reaction of calcium carbide with water to produce a steady supply of acetylene, which was ignited to provide a portable lantern.



19th-century miner's lamp. The lamp uses burning acetylene, produced by the slow reaction of calcium carbide with water, to provide light.

The reaction of carbon with most transition metals at high temperatures produces interstitial carbides. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal–carbon interactions, which result in different properties: most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range. Among the most important are tungsten carbide (WC), which is used industrially in high-speed cutting tools, and cementite ($Fe_3C$), which is a major component of steel.

Elements with an electronegativity similar to that of carbon form covalent carbides, such as silicon carbide (SiC; Equation ???) and boron carbide ($B_4C$). These substances are extremely hard, have high melting points, and are chemically inert. For example, silicon carbide is highly resistant to chemical attack at temperatures as high as 1600°C. Because it also maintains its strength at high temperatures, silicon carbide is used in heating elements for electric furnaces and in variable-temperature resistors.

> *Carbides formed from group 1 and 2 elements are ionic. Transition metals form interstitial carbides with covalent metal–carbon interactions, and covalent carbides are chemically inert.*

**Example 21.2.1**

For each reaction, explain why the given product forms.

a. $CO(g) + Cl_2(g) \rightarrow Cl_2C{=}O(g)$
b. $CO(g) + BF_3(g) \rightarrow F_3B{:}C{\equiv}O(g)$

c. $Sr(s) + 2C(s) \xrightarrow{\Delta} SrC_2(s)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

**Solution**

a. Because the carbon in CO is in an intermediate oxidation state (+2), CO can be either a reductant or an oxidant; it is also a Lewis base. The other reactant ($Cl_2$) is an oxidant, so we expect a redox reaction to occur in which the carbon of CO is further oxidized. Because $Cl_2$ is a two-electron oxidant and the carbon atom of CO can be oxidized by two electrons to the +4 oxidation state, the product is phosgene ($Cl_2C{=}O$).
b. Unlike $Cl_2$, $BF_3$ is not a good oxidant, even though it contains boron in its highest oxidation state (+3). Nor can $BF_3$ behave like a reductant. Like any other species with only six valence electrons, however, it is certainly a Lewis acid. Hence an acid–base reaction is the most likely alternative, especially because we know that CO can use the lone pair of electrons on carbon to act as a Lewis base. The most probable reaction is therefore the formation of a Lewis acid–base adduct.
c. Typically, both reactants behave like reductants. Unless one of them can also behave like an oxidant, no reaction will occur. We know that Sr is an active metal because it lies far to the left in the periodic table and that it is more electropositive than carbon. Carbon is a nonmetal with a significantly higher electronegativity; it is therefore more likely to accept electrons in a redox reaction. We conclude, therefore, that Sr will be oxidized, and C will be reduced. Carbon forms ionic carbides with active metals, so the reaction will produce a species formally containing either $C^{4-}$ or $C_2^{2-}$. Those that contain $C^{4-}$ usually involve small, highly charged metal ions, so $Sr^{2+}$ will produce the acetylide ($SrC_2$) instead.

**? Exercise 21.2.1**

Predict the products of the reactions and write a balanced chemical equation for each reaction.

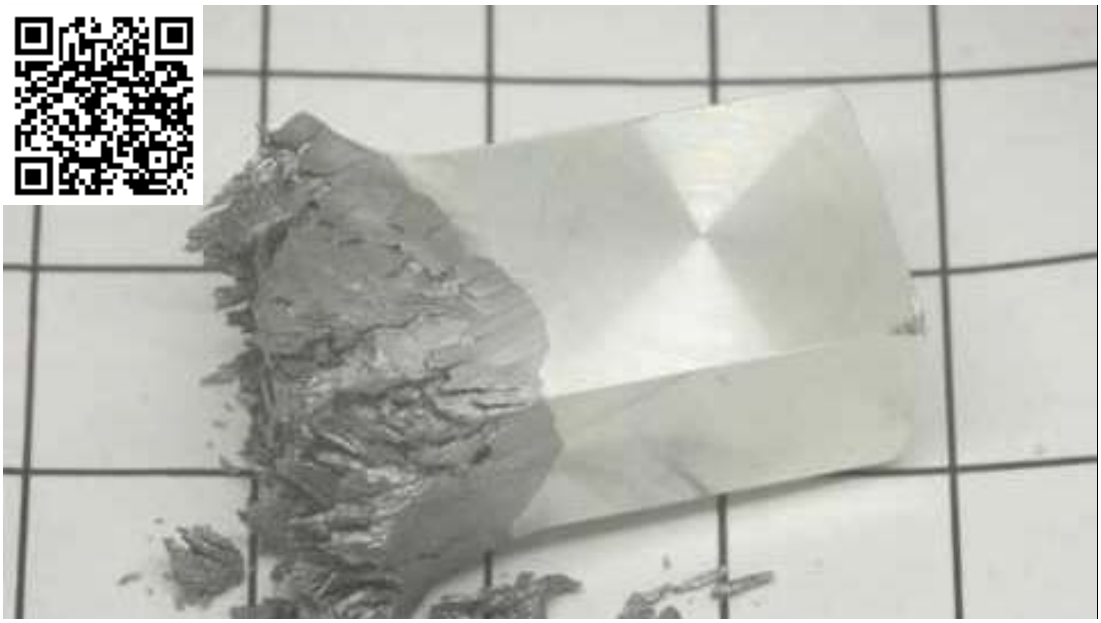
a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta}$
b. $C(s) + H_2O(l) \rightarrow$
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow$

**Answer**

a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta} CO_2(g)$
b. $C(s) + H_2O(l) \rightarrow$ no reaction
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow CO_2(g) + NaHSO_4(aq) + H_2O(l)$

## Reactions and Compounds of the Heavier Group 14 Elements

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2°C, and the nonmetallic α form is stable below 13.2°C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.



***Video*** 21.2.1*: Time lapse tin pest reaction.*

Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable $SiF_6^{2-}$ ion. Germanium is more metallic in its behavior than silicon. For example, it dissolves in hot oxidizing acids, such as $HNO_3$ and $H_2SO_4$, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a $Pb^{2+}$ salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus $CCl_2$ is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; $SiCl_2$ can be isolated at very low temperatures, but it decomposes rapidly above −150°C, and $GeCl_2$ is relatively stable at temperatures below 20°C. In contrast, $SnCl_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

> *The stability of the group 14 dichlorides increases dramatically from carbon to lead.*

Although the first four elements of group 14 form tetrahalides ($MX_4$) with all the halogens, only fluorine is able to oxidize lead to the +4 oxidation state, giving $PbF_4$. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \tag{21.2.11}$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions. Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14 elements with excess $O_2$ or $S_8$ gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

> *The dioxides of the group 14 elements become increasingly basic down the group.*

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. The relative strengths of the C–O and Si–O bonds contradict the generalization that bond strengths decrease as the bonded atoms become larger. This is because we have thus far assumed that a formal single bond between two atoms can always be described in terms of a single pair of shared electrons. In the case of Si–O bonds, however, the presence of relatively low-energy, empty d orbitals on Si and nonbonding electron pairs in the p or $sp^n$ hybrid orbitals of O results in a partial π bond (Figure 21.2.3). Due to its partial π double bond character, the Si–O bond is significantly stronger and shorter than would otherwise be expected. A

similar interaction with oxygen is also an important feature of the chemistry of the elements that follow silicon in the third period (P, S, and Cl). Because the Si–O bond is unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

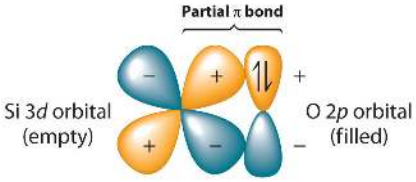
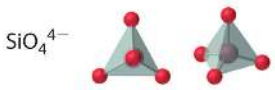


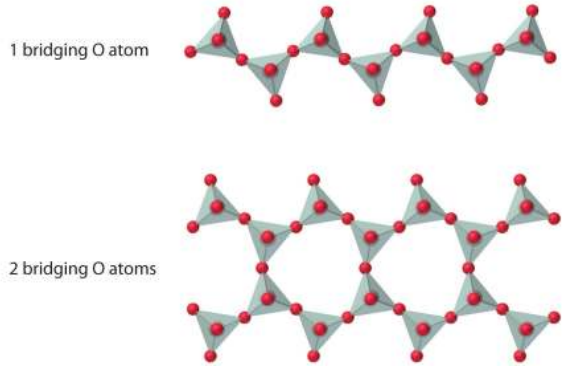

Figure 21.2.3: $\pi$ Bonding between Silicon and Oxygen. Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2p hybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond character and making it significantly stronger (and shorter) than expected for a single bond.

> *Because silicon–oxygen bonds are unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.*

Compounds with anions that contain only silicon and oxygen are called silicates, whose basic building block is the $SiO_4^{4-}$ unit:




The number of oxygen atoms shared between silicon atoms and the way in which the units are linked vary considerably in different silicates. Converting one of the oxygen atoms from terminal to bridging generates chains of silicates, while converting two oxygen atoms from terminal to bridging generates double chains. In contrast, converting three or four oxygens to bridging generates a variety of complex layered and three-dimensional structures, respectively.




In a large and important class of materials called aluminosilicates, some of the Si atoms are replaced by Al atoms to give aluminosilicates such as zeolites, whose three-dimensional framework structures have large cavities connected by smaller tunnels (Figure 21.2.4). Because the cations in zeolites are readily exchanged, zeolites are used in laundry detergents as water-softening agents: the more loosely bound $Na^+$ ions inside the zeolite cavities are displaced by the more highly charged $Mg^{2+}$ and $Ca^{2+}$ ions present in hard water, which bind more tightly. Zeolites are also used as catalysts and for water purification.

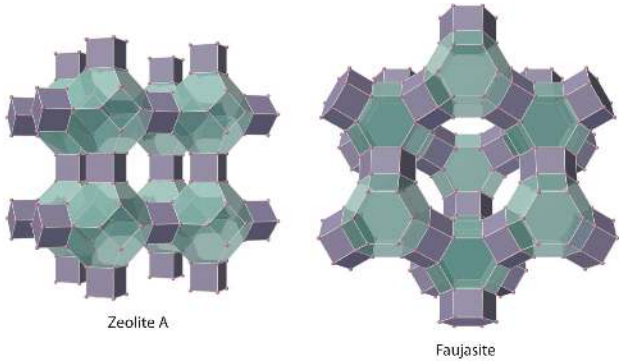



Figure 21.2.4: Zeolites Are Aluminosilicates with Large Cavities Connected by Channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities differ in different types of zeolites. For example, in zeolite A the aluminosilicate cages are arranged in a cubic fashion, and the channels connecting the cavities intersect at right angles. In contrast, the cavities in faujasite are much larger, and the channels intersect at 120° angles. In these idealized models, the oxygen atoms that connect each pair of silicon atoms have been omitted.

Silicon and germanium react with nitrogen at high temperature to form nitrides ($M_3N_4$):

$$3Si_{(l)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \tag{21.2.12}$$

Silicon nitride has properties that make it suitable for high-temperature engineering applications: it is strong, very hard, and chemically inert, and it retains these properties to temperatures of about 1000°C.

Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Although metal silicides have structures that are as complex as those of the metal borides and carbides, few silicides are structurally similar to the corresponding borides due to the significantly larger size of Si (atomic radius 111 pm versus 87 pm for B). Silicides of active metals, such as $Mg_2Si$, are ionic compounds that contain the $Si^{4-}$ ion. They react with aqueous acid to form silicon hydrides such as $SiH_4$:

$$Mg_2Si_{(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiH_{4(g)} \tag{21.2.13}$$

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched silanes (analogous to alkanes) are known up to only n = 10; the germanium analogues (germanes) are known up to n = 9. In contrast, the only known hydride of tin is $SnH_4$, and it slowly decomposes to elemental Sn and $H_2$ at room temperature. The simplest lead hydride ($PbH_4$) is so unstable that chemists are not even certain it exists. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown. Silicon-based life-forms are therefore likely to be found only in science fiction.

> *The stability of group 14 hydrides decreases down the group, and E=E and E≡E bonds become weaker.*

The only important organic derivatives of lead are compounds such as tetraethyllead [$(CH_3CH_2)_4Pb$]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·), which can be used to control the rate of combustion reactions. For 60 yr, hundreds of thousands of tons of lead were burned annually in automobile engines, producing a mist of lead oxide particles along the highways that constituted a potentially serious public health problem. (Example 6 in Section 22.3 examines this problem.) The use of catalytic converters reduced the amount of carbon monoxide, nitrogen oxides, and hydrocarbons released into the atmosphere through automobile exhausts, but it did nothing to decrease lead emissions. Because lead poisons catalytic converters, however, its use as a gasoline additive has been banned in most of the world.

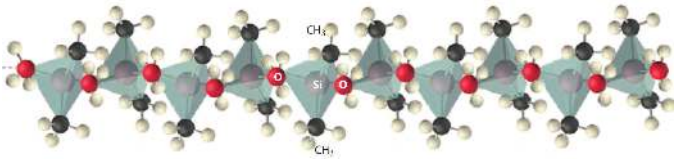


Figure 21.2.5 Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups ($–CH_3$) shown here. The terminal silicon atoms are bonded to three methyl groups. Silicones can be oily, waxy, flexible, or elastic, depending on the chain length, the extent of cross-linking between the chains, and the type of organic group.

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called silicones contain an $(Si–O–)_n$ backbone with organic groups attached to Si (Figure 21.2.5). The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials, such as the plastic substance known as Silly Putty.



A child playing with Silly Putty, a silicone polymer with unusual mechanical properties. Gentle pressure causes Silly Putty to flow or stretch, but it cannot be flattened when hit with a hammer. This is called a "Non-Newtonian Fluid"

## Example 21.2.2

For each reaction, explain why the given products form.

a. $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$
b. $Mg_2Si(s) + 4H_2O(l) \rightarrow SiH_4(g) + 2Mg(OH)_2(s)$
c. $GeO_2(s) + 4OH^-(aq) \rightarrow GeO_4^{4-}(aq) + 2H_2O(l)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

**Solution**

a. Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, $Pb^{4+}$ is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect $PbCl_2$ to be the product.
b. This is the reaction of water with a metal silicide, which formally contains the $Si^{4-}$ ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid–base reaction to occur in which water acts as an acid. Because $Mg_2Si$ contains Si in its lowest possible oxidation state, however, an oxidation–reduction reaction is also a possibility. But water is a relatively weak oxidant, so an acid–base reaction is more likely. The acid ($H_2O$) transfers a proton to the base ($Si^{4-}$), which can accept four protons to form $SiH_4$. Proton transfer from water produces the $OH^-$ ion, which will combine with $Mg^{2+}$ to give magnesium hydroxide.

c. We expect germanium dioxide ($GeO_2$) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in strong aqueous base to give an anionic species analogous to silicate.

**? Exercise 21.2.2**

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $PbO_2(s) \xrightarrow{\Delta}$
b. $GeCl_4(s) + H_2O(l) \rightarrow$
c. $Sn(s) + HCl(aq) \rightarrow$

**Answer**

a. $PbO_2(s) \xrightarrow{\Delta} PbO(s) + \frac{1}{2}O_2(g)$
b. $GeCl_4(s) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(aq)$
c. $Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + H_2(g) + 2Cl^-(aq)$

## Summary

The group 14 elements show the greatest diversity in chemical behavior of any group; covalent bond strengths decease with increasing atomic size, and ionization energies are greater than expected, increasing from C to Pb. The group 14 elements show the greatest range of chemical behavior of any group in the periodic table. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionization energies due to an increase in $Z_{eff}$, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap and steric crowding. Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and $C^{4-}$ (methide) or $C_2^{2-}$ (acetylide) anions; interstitial carbides, which are characterized by covalent metal–carbon interactions and are among the hardest substances known; and covalent carbides, which have three-dimensional covalent network structures that make them extremely hard, high melting, and chemically inert. Consistent with periodic trends, metallic behavior increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms; aluminosilicates with three-dimensional framework structures are called zeolites. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides become thermodynamically less stable down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain an Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

## Contributors and Attributions

- Anonymous

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# 21.3: The Elements of Group 15 (The Pnicogens)

**Learning Objectives**

- To understand the trends in properties and reactivity of the group 15 elements: the pnicogens.

Like the group 14 elements, the lightest member of group 15, nitrogen, is found in nature as the free element, and the heaviest elements have been known for centuries because they are easily isolated from their ores. Antimony (Sb) was probably the first of the pnicogens to be obtained in elemental form and recognized as an element. Its atomic symbol comes from its Roman name: stibium. It is found in stibnite ($Sb_2S_3$), a black mineral that has been used as a cosmetic (an early form of mascara) since biblical times, and it is easily reduced to the metal in a charcoal fire (Figure 21.3.1). The Egyptians used antimony to coat copper objects as early as the third millennium BC, and antimony is still used in alloys to improve the tonal quality of bells.

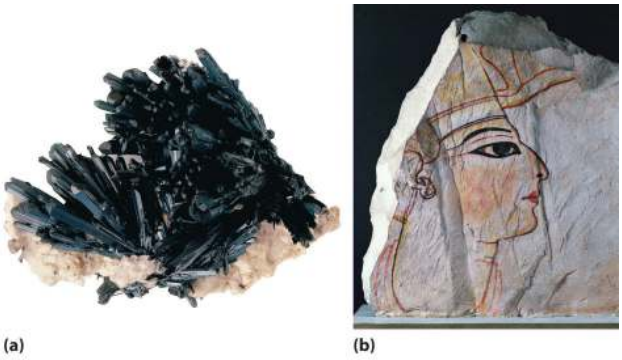



Figure 21.3.1: The Ancient Egyptians Used Finely Ground Antimony Sulfide for Eye Makeup. (a) Crystals of the soft black mineral stibnite ($Sb_2S_3$) on a white mineral matrix. (b) A fragment of an Egyptian painting on limestone from the 16th–13th centuries BC shows the use of ground stibnite ("kohl") as black eye shadow. Small vases of ground stibnite have been found among the funeral goods buried with Egyptian pharaohs.

In the form of its yellow sulfide ore, orpiment ($As_2S_3$), arsenic (As) has been known to physicians and professional assassins since ancient Greece, although elemental arsenic was not isolated until centuries later. The history of bismuth (Bi), in contrast, is more difficult to follow because early alchemists often confused it with other metals, such as lead, tin, antimony, and even silver (due to its slightly pinkish-white luster). Its name comes from the old German wismut, meaning "white metal." Bismuth was finally isolated in the 15th century, and it was used to make movable type for printing shortly after the invention of the Gutenberg printing process in 1440. Bismuth is used in printing because it is one of the few substances known whose solid state is less dense than the liquid. Consequently, its alloys expand as they cool, filling a mold completely and producing crisp, clear letters for typesetting.

Phosphorus was discovered in 1669 by the German alchemist Hennig Brandt, who was looking for the "philosophers' stone," a mythical substance capable of converting base metals to silver or gold. Believing that human urine was the source of the key ingredient, Brandt obtained several dozen buckets of urine, which he allowed to putrefy. The urine was distilled to dryness at high temperature and then condensed; the last fumes were collected under water, giving a waxy white solid that had unusual properties. For example, it glowed in the dark and burst into flames when removed from the water. (Unfortunately for Brandt, however, it did not turn lead into gold.) The element was given its current name (from the Greek phos, meaning "light," and phoros, meaning "bringing") in the 17th century. For more than a century, the only way to obtain phosphorus was the distillation of urine, but in 1769 it was discovered that phosphorus could be obtained more easily from bones. During the 19th century, the demand for phosphorus for matches was so great that battlefields and paupers' graveyards were systematically scavenged for bones. Early matches were pieces of wood coated with elemental phosphorus that were stored in an evacuated glass tube and ignited when the tube was broken (which could cause unfortunate accidents if the matches were kept in a pocket!).

Unfortunately, elemental phosphorus is volatile and highly toxic. It is absorbed by the teeth and destroys bone in the jaw, leading to a painful and fatal condition called "phossy jaw," which for many years was accepted as an occupational hazard of working in the match industry.

Although nitrogen is the most abundant element in the atmosphere, it was the last of the pnicogens to be obtained in pure form. In 1772, Daniel Rutherford, working with Joseph Black (who discovered $CO_2$), noticed that a gas remained when $CO_2$ was removed

from a combustion reaction. Antoine Lavoisier called the gas azote, meaning “no life,” because it did not support life. When it was discovered that the same element was also present in nitric acid and nitrate salts such as $KNO_3$ (nitre), it was named nitrogen. About 90% of the nitrogen produced today is used to provide an inert atmosphere for processes or reactions that are oxygen sensitive, such as the production of steel, petroleum refining, and the packaging of foods and pharmaceuticals.

## Preparation and General Properties of the Group 15 Elements

Because the atmosphere contains several trillion tons of elemental nitrogen with a purity of about 80%, it is a huge source of nitrogen gas. Distillation of liquefied air yields nitrogen gas that is more than 99.99% pure, but small amounts of very pure nitrogen gas can be obtained from the thermal decomposition of sodium azide:

$$2\mathrm{NaN_3(s)} \xrightarrow{\Delta} 2\mathrm{Na(l)} + 3\mathrm{N_2(g)} \tag{21.3.1}$$

In contrast, Earth’s crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of $KNO_3$ and $NaNO_3$ in the deserts of Chile and Russia, which were apparently formed when ancient alkaline lakes evaporated. Consequently, virtually all nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Phosphorus, which constitutes only about 0.1% of Earth’s crust, is much more abundant in ores than nitrogen. Like aluminum and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.

The other three pnicogens are much less abundant: arsenic is found in Earth’s crust at a concentration of about 2 ppm, antimony is an order of magnitude less abundant, and bismuth is almost as rare as gold. All three elements have a high affinity for the chalcogens and are usually found as the sulfide ores ($M_2S_3$), often in combination with sulfides of other heavy elements, such as copper, silver, and lead. Hence a major source of antimony and bismuth is flue dust obtained by smelting the sulfide ores of the more abundant metals.

In group 15, as elsewhere in the p block, we see large differences between the lightest element (N) and its congeners in size, ionization energy, electron affinity, and electronegativity (Table 21.3.1). The chemical behavior of the elements can be summarized rather simply: nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. With their $ns^2np^3$ valence electron configurations, all form compounds by losing either the three np valence electrons to form the +3 oxidation state or the three np and the two ns valence electrons to give the +5 oxidation state, whose stability decreases smoothly from phosphorus to bismuth. In addition, the relatively large magnitude of the electron affinity of the lighter pnicogens enables them to form compounds in the −3 oxidation state (such as $NH_3$ and $PH_3$), in which three electrons are formally added to the neutral atom to give a filled np subshell. Nitrogen has the unusual ability to form compounds in nine different oxidation states, including −3, +3, and +5. Because neutral covalent compounds of the trivalent pnicogens contain a lone pair of electrons on the central atom, they tend to behave as Lewis bases.

Table 21.3.1: Selected Properties of the Group 15 Elements

| Property | Nitrogen | Phosphorus | Arsenic | Antimony | Bismuth |
|---|---|---|---|---|---|
| atomic symbol | N | P | As | Sb | Bi |
| atomic number | 7 | 15 | 33 | 51 | 83 |
| atomic mass (amu) | 14.01 | 30.97 | 74.92 | 121.76 | 209.98 |
| valence electron configuration* | $2s^2 2p^3$ | $3s^2 3p^3$ | $4s^2 4p^3$ | $5s^2 5p^3$ | $6s^2 6p^3$ |
| melting point/boiling point (°C) | −210/−196 | 44.15/281[c] | 817 (at 3.70 MPa)/603 (sublimes)[†] | 631/1587 | 271/1564 |
| density (g/cm$^3$) at 25°C | 1.15 (g/L) | 1.82[†] | 5.75[‡] | 6.68 | 9.79 |
| atomic radius (pm) | 56 | 98 | 114 | 133 | 143 |
| first ionization energy (kJ/mol) | 1402 | 1012 | 945 | 831 | 703 |
| common oxidation state(s) | −3 to +5 | +5, +3, −3 | +5, +3 | +5, +3 | +3 |
| ionic radius (pm)[§] | 146 (−3), 16 (+3) | 212 (−3), 44 (+3) | 58 (+3) | 76 (+3), 60 (+5) | 103 (+3) |
| electron affinity (kJ/mol) | 0 | −72 | −78 | −101 | −91 |
| electronegativity | 3.0 | 2.2 | 2.2 | 2.1 | 1.9 |
| standard reduction potential (E°, V) ($E^V \rightarrow E^{III}$ in acidic solution)[‖] | +0.93 | −0.28 | +0.56 | +0.65 | — |
| product of reaction with $O_2$ | $NO_2$, NO | $P_4O_6$, $P_4O_{10}$ | $As_4O_6$ | $Sb_2O_5$ | $Bi_2O_3$ |
| type of oxide | acidic ($NO_2$), neutral (NO, $N_2O$) | acidic | acidic | amphoteric | basic |
| product of reaction with $N_2$ | — | none | none | none | none |
| product of reaction with $X_2$ | none | $PX_3$, $PX_5$ | $AsF_5$, $AsX_3$ | $SbF_5$, $SbCl_5$, $SbBr_3$, $SbI_3$ | $BiF_5$, $BiX_3$ |
| product of reaction with $H_2$ | none | none | none | none | none |

*The configuration shown does not include filled d and f subshells. [†]For white phosphorus. [‡]For gray arsenic. [§]The values cited are for six-coordinate ions in the indicated oxidation states. The $N^{5+}$, $P^{5+}$, and $As^{5+}$ ions are not known species. [‖]The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2\,H^+ + 2\,e^- \longrightarrow H_3EO_3 + H_2O$; and for Sb it is $Sb_2O_5 + 4\,e^- + 10\,H^+ \longrightarrow 2\,Sb^{3+} + 5\,H_2O$.

> *In group 15, the stability of the +5 oxidation state decreases from P to Bi.*

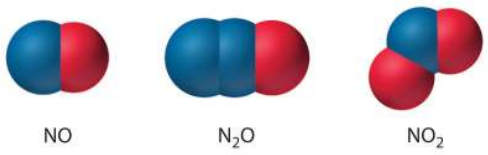
> *Because neutral covalent compounds of the trivalent group 15 elements have a lone pair of electrons on the central atom, they tend to be Lewis bases.*

## Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in at most four electron-pair bonds by using $sp^3$ hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of repulsive interactions between lone pairs of electrons on adjacent atoms. These interactions become important at the shorter internuclear distances encountered with the smaller, second-period elements of groups 15, 16, and 17. Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion ($N_3^-$).

Nitrogen is the only pnicogen that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is $N_2$, whose N≡N bond is so strong ($D_{N≡N}$ = 942 kJ/mol) compared with the N–N and N=N bonds ($D_{N–N}$ = 167 kJ/mol; $D_{N=N}$ = 418 kJ/mol) that all compounds containing N–N and N=N bonds are thermodynamically unstable with respect to the formation of $N_2$. In fact, the formation of the N≡N bond is so thermodynamically favored that virtually all compounds containing N–N bonds are potentially explosive.

Again in contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium nitride, and it is reduced to ammonia by certain microorganisms. At higher temperatures, however, $N_2$ reacts with more electropositive elements, such as those in group 13, to give binary nitrides, which range from covalent to ionic in character. Like the corresponding compounds of carbon, binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances.




Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, $N_2$ reacts with $H_2$ to form ammonia, with $O_2$ to form a mixture of NO and $NO_2$, and with carbon to form cyanogen (N≡C–C≡N); elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides ($NX_3$) are known. Except for $NF_3$, all are toxic, thermodynamically unstable, and potentially explosive, and all are prepared by reacting the halogen with $NH_3$ rather than $N_2$. Both nitrogen monoxide (NO) and nitrogen dioxide ($NO_2$) are thermodynamically unstable, with positive free energies of formation. Unlike NO, $NO_2$ reacts readily with excess water, forming a 1:1 mixture of nitrous acid ($HNO_2$) and nitric acid ($HNO_3$):

$$2\,NO_2\,(g) + H_2O\,(l) \rightarrow HNO_2\,(aq) + HNO_3\,(aq) \tag{21.3.2}$$

Nitrogen also forms $N_2O$ (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with $CO_2$ and can be represented as $^-N{=}N^+{=}O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:

> *Few binary molecular compounds of nitrogen are formed by the direct reaction of the elements.*

At elevated temperatures, nitrogen reacts with highly electropositive metals to form ionic nitrides, such as $Li_3N$ and $Ca_3N_2$. These compounds consist of ionic lattices formed by $M^{n+}$ and $N^{3-}$ ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, with less electropositive metals nitrogen forms a range of interstitial nitrides, in which nitrogen occupies holes in a close-packed metallic structure. Like the interstitial carbides and borides, these substances are typically very hard, high-melting materials that have metallic luster and conductivity.

Nitrogen also reacts with semimetals at very high temperatures to produce covalent nitrides, such as $Si_3N_4$ and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials.

Ammonia ($NH_3$) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an $O_2$ atmosphere:

$$4\,NH_3\,(g) + 3\,O_2\,(g) \rightarrow 2\,N_2\,(g) + 6\,H_2O\,(g) \tag{21.3.3}$$

About 10% of the ammonia produced annually is used to make fibers and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives, such as ammonium nitrate, TNT (trinitrotoluene), and nitroglycerine. Large amounts of anhydrous liquid ammonia are used as fertilizer.

Nitrogen forms two other important binary compounds with hydrogen. Hydrazoic acid ($HN_3$), also called hydrogen azide, is a colorless, highly toxic, and explosive substance. Hydrazine ($N_2H_4$) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

> *B, C, and N all react with transition metals to form interstitial compounds that are hard, high-melting materials.*

## Example 21.3.1

For each reaction, explain why the given products form when the reactants are heated.

a. $Sr(s) + N_2O(g) \xrightarrow{\Delta} SrO(s) + N_2(g)$
b. $NH_4NO_2(s) \xrightarrow{\Delta} N_2(g) + 2H_2O(g)$
c. $Pb(NO_3)_2(s) \xrightarrow{\Delta} PbO_2(s) + 2NO_2(g)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

**Solution**

a. As an alkali metal, strontium is a strong reductant. If the other reactant can act as an oxidant, then a redox reaction will occur. Nitrous oxide contains nitrogen in a low oxidation state (+1), so we would not normally consider it an oxidant. Nitrous oxide is, however, thermodynamically unstable ($\Delta H°_f > 0$ and $\Delta G°_f > 0$), and it can be reduced to $N_2$, which is a stable species. Consequently, we predict that a redox reaction will occur.
b. When a substance is heated, a decomposition reaction probably will occur, which often involves the release of stable gases. In this case, ammonium nitrite contains nitrogen in two different oxidation states (−3 and +3), so an internal redox reaction is a possibility. Due to its thermodynamic stability, $N_2$ is the probable nitrogen-containing product, whereas we predict that H and O will combine to form $H_2O$.
c. Again, this is probably a thermal decomposition reaction. If one element is in an usually high oxidation state and another in a low oxidation state, a redox reaction will probably occur. Lead nitrate contains the $Pb^{2+}$ cation and the nitrate anion, which contains nitrogen in its highest possible oxidation state (+5). Hence nitrogen can be reduced, and we know that lead can be oxidized to the +4 oxidation state. Consequently, it is likely that lead(II) nitrate will decompose to lead(IV) oxide and nitrogen dioxide when heated. Even though $PbO_2$ is a powerful oxidant, the release of a gas such as $NO_2$ can often drive an otherwise unfavorable reaction to completion (Le Chatelier's principle). Note, however, that $PbO_2$ will probably decompose to PbO at high temperatures.

## Exercise 23.3.1

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $NO(g) + H_2O(l) \xrightarrow{\Delta}$
b. $NH_4NO_3(s) \xrightarrow{\Delta}$

c. $Sr(s) + N_2(g) \rightarrow$

**Answer**

a. $NO(g) + H_2O(l) \xrightarrow{\Delta}$ no reaction
b. $NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$
c. $3Sr(s) + N_2(g) \rightarrow Sr_3N_2(s)$

## Reactions and Compounds of the Heavier Pnicogens

Like the heavier elements of group 14, the heavier pnicogens form catenated compounds that contain only single bonds, whose stability decreases rapidly as we go down the group. For example, phosphorus exists as multiple allotropes, the most common of which is white phosphorus, which consists of $P_4$ tetrahedra and behaves like a typical nonmetal. As is typical of a molecular solid, white phosphorus is volatile, has a low melting point (44.1°C), and is soluble in nonpolar solvents. It is highly strained, with bond angles of only 60°, which partially explains why it is so reactive and so easily converted to more stable allotropes. Heating white phosphorus for several days converts it to red phosphorus, a polymer that is air stable, virtually insoluble, denser than white phosphorus, and higher melting, properties that make it much safer to handle. A third allotrope of phosphorus, black phosphorus, is prepared by heating the other allotropes under high pressure; it is even less reactive, denser, and higher melting than red phosphorus. As expected from their structures, white phosphorus is an electrical insulator, and red and black phosphorus are semiconductors. The three heaviest pnicogens—arsenic, antimony, and bismuth—all have a metallic luster, but they are brittle (not ductile) and relatively poor electrical conductors.

> *As in group 14, the heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases as we go down the group.*

The reactivity of the heavier pnicogens decreases as we go down the column. Phosphorus is by far the most reactive of the pnicogens, forming binary compounds with every element in the periodic table except antimony, bismuth, and the noble gases. Phosphorus reacts rapidly with $O_2$, whereas arsenic burns in pure $O_2$ if ignited, and antimony and bismuth react with $O_2$ only when heated. None of the pnicogens reacts with nonoxidizing acids such as aqueous HCl, but all dissolve in oxidizing acids such as $HNO_3$. Only bismuth behaves like a metal, dissolving in $HNO_3$ to give the hydrated $Bi^{3+}$ cation.

> *The reactivity of the heavier group 15 elements decreases as we go down the column.*

The heavier pnicogens can use energetically accessible 3d, 4d, or 5d orbitals to form $dsp^3$ or $d^2sp^3$ hybrid orbitals for bonding. Consequently, these elements often have coordination numbers of 5 or higher. Phosphorus and arsenic form halides (e.g., $AsCl_5$) that are generally covalent molecular species and behave like typical nonmetal halides, reacting with water to form the corresponding oxoacids (in this case, $H_3AsO_4$). All the pentahalides are potent Lewis acids that can expand their coordination to accommodate the lone pair of a Lewis base:

$$AsF_5(soln) + F^-(soln) \rightarrow AsF_6^-(soln) \tag{21.3.4}$$

In contrast, bismuth halides have extended lattice structures and dissolve in water to produce hydrated ions, consistent with the stronger metallic character of bismuth.

Except for $BiF_3$, which is essentially an ionic compound, the trihalides are volatile covalent molecules with a lone pair of electrons on the central atom. Like the pentahalides, the trihalides react rapidly with water. In the cases of phosphorus and arsenic, the products are the corresponding acids, $H_3PO_3$ and $H_3AsO_3$, where E is P or As:

$$EX_3(l) + 3H_2O(l) \rightarrow H_3EO_3(aq) + 3HX(aq) \tag{21.3.5}$$

Phosphorus halides are also used to produce insecticides, flame retardants, and plasticizers.

> *Phosphorus has the greatest ability to form π bonds with elements such as O, N, and C.*

With energetically accessible d orbitals, phosphorus and, to a lesser extent, arsenic are able to form π bonds with second-period atoms such as N and O. This effect is even more important for phosphorus than for silicon, resulting in very strong P–O bonds and even stronger P=O bonds. The first four elements in group 15 also react with oxygen to produce the corresponding oxide in the +3

oxidation state. Of these oxides, $P_4O_6$ and $As_4O_6$ have cage structures formed by inserting an oxygen atom into each edge of the $P_4$ or $As_4$ tetrahedron (part (a) in Figure 21.3.2), and they behave like typical nonmetal oxides. For example, $P_4O_6$ reacts with water to form phosphorous acid ($H_3PO_3$). Consistent with its position between the nonmetal and metallic oxides, $Sb_4O_6$ is amphoteric, dissolving in either acid or base. In contrast, $Bi_2O_3$ behaves like a basic metallic oxide, dissolving in acid to give solutions that contain the hydrated $Bi^{3+}$ ion. The two least metallic elements of the heavier pnicogens, phosphorus and arsenic, form very stable oxides with the formula $E_4O_{10}$ in the +5 oxidation state (part (b) in Figure 21.3.2. In contrast, $Bi_2O_5$ is so unstable that there is no absolute proof it exists.

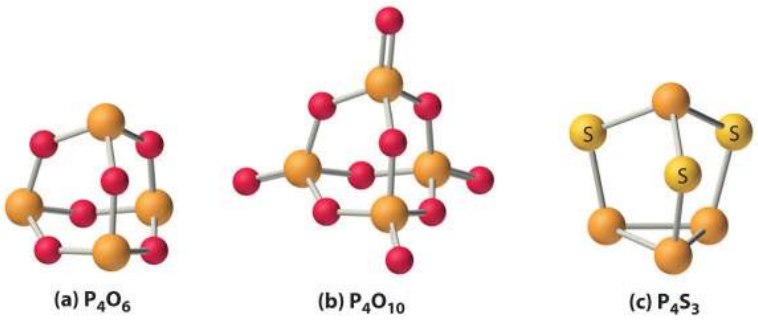



Figure 21.3.2: The Structures of Some Cage Compounds of Phosphorus. (a, b) The structures of $P_4O_6$ and $P_4O_{10}$ are both derived from the structure of white phosphorus ($P_4$) by inserting an oxygen atom into each of the six edges of the $P_4$ tetrahedron; $P_4O_{10}$ contains an additional terminal oxygen atom bonded to each phosphorus atom. (c) The structure of $P_4S_3$ is also derived from the structure of $P_4$ by inserting three sulfur atoms into three adjacent edges of the tetrahedron.

The heavier pnicogens form sulfides that range from molecular species with three-dimensional cage structures, such as $P_4S_3$ (part (c) in Figure 21.3.2), to layered or ribbon structures, such as $Sb_2S_3$ and $Bi_2S_3$, which are semiconductors. Reacting the heavier pnicogens with metals produces substances whose properties vary with the metal content. Metal-rich phosphides (such as $M_4P$) are hard, high-melting, electrically conductive solids with a metallic luster, whereas phosphorus-rich phosphides (such as $MP_{15}$) are lower melting and less thermally stable because they contain catenated $P_n$ units. Many organic or organometallic compounds of the heavier pnicogens containing one to five alkyl or aryl groups are also known. Because of the decreasing strength of the pnicogen–carbon bond, their thermal stability decreases from phosphorus to bismuth.

> *The thermal stability of organic or organometallic compounds of group 15 decreases down the group due to the decreasing strength of the pnicogen–carbon bond.*

## Example 21.3.2

For each reaction, explain why the given products form.

a. $Bi(s) + \frac{3}{2}Br(l) \rightarrow BiBr_3(s)$
b. $2(CH_3)_3As(l) + O_2(g) \rightarrow 2(CH_3)_3As{=}O(s)$
c. $PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(aq)$
d. $As(s) + Ga(s) \xrightarrow{\Delta} GaAs(s)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

**Solution**

a. Bromine is an oxidant, and bismuth is a metal that can be oxidized. Hence a redox reaction is likely to occur. To identify the product, recall that bismuth can form compounds in either the +3 or +5 oxidation state. The heaviest pnicogen, bismuth is rather difficult to oxidize to the +5 oxidation state because of the inert-pair effect. Hence the product will probably be bismuth(III) bromide.

b. Trimethylarsine, with a lone pair of electrons on the arsenic atom, can act as either a Lewis base or a reductant. If arsenic is oxidized by two electrons, then oxygen must be reduced, most probably by two electrons to the −2 oxidation state. Because As(V) forms strong bonds to oxygen due to π bonding, the expected product is $(CH_3)_3As{=}O$.
c. Phosphorus tribromide is a typical nonmetal halide. We expect it to react with water to produce an oxoacid of P(III) and the corresponding hydrohalic acid.Because of the strength of the P=O bond, phosphorous acid ($H_3PO_3$) is actually $HP(O)(OH)_2$, which contains a P=O bond and a P–H bond.
d. Gallium is a metal with a strong tendency to act as a reductant and form compounds in the +3 oxidation state. In contrast, arsenic is a semimetal. It can act as a reductant to form compounds in the +3 or +5 oxidation state, or it can act as an oxidant, accepting electrons to form compounds in the −3 oxidation state. If a reaction occurs, then a binary compound will probably form with a 1:1 ratio of the elements. GaAs is an example of a III-V compound, many of which are used in the electronics industry.

**? Exercise 21.3.2**

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $PCl_5(s) + H_2O(l) \rightarrow$
b. $Bi_2O_5(s) \xrightarrow{\Delta}$
c. $Ca_3P_2(s) + H^+(aq) \rightarrow$
d. $NaNH_2(s) + PH_3(soln) \rightarrow$

**Answer**

a. $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$
b. $Bi_2O_5(s) \xrightarrow{\Delta} Bi_2O_3(s) + O_2(g)$
c. $Ca_3P_2(s) + 6H^+(aq) \rightarrow 2PH_3(g) + 3Ca^{2+}(aq)$
d. $NaNH_2(s) + PH_3(soln) \rightarrow NaPH_2(s) + NH_3(soln)$

## Summary

The reactivity of the heavier group 15 elements decreases down the group, as does the stability of their catenated compounds. In group 15, nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. Nitrogen forms compounds in nine different oxidation states. The stability of the +5 oxidation state decreases from phosphorus to bismuth because of the inert-pair effect. Due to their higher electronegativity, the lighter pnicogens form compounds in the −3 oxidation state. Because of the presence of a lone pair of electrons on the pnicogen, neutral covalent compounds of the trivalent pnicogens are Lewis bases. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it does form multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic in character. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides. The reactivity of the pnicogens decreases with increasing atomic number. Compounds of the heavier pnicogens often have coordination numbers of 5 or higher and use $dsp^3$ or $d^2sp^3$ hybrid orbitals for bonding. Because phosphorus and arsenic have energetically accessible d orbitals, these elements form π bonds with second-period atoms such as O and N. Phosphorus reacts with metals to produce phosphides. Metal-rich phosphides are hard, high-melting, electrically conductive solids with metallic luster, whereas phosphorus-rich phosphides, which contain catenated phosphorus units, are lower melting and less thermally stable.

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# 21.4: The Elements of Group 16 (The Chalcogens)

**Learning Objectives**

- To understand the trends in properties and reactivity of the group 16 elements: the chalcogens.

The chalcogens are the first group in the p block to have no stable metallic elements. All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can even be described as a semimetal. As in groups 14 and 15, the lightest element of group 16, oxygen, is found in nature as the free element.

Of the group 16 elements, only sulfur was known in ancient times; the others were not discovered until the late 18th and 19th centuries. Sulfur is frequently found as yellow crystalline deposits of essentially pure $S_8$ in areas of intense volcanic activity or around hot springs. As early as the 15th century BC, sulfur was used as a fumigant in Homeric Greece because, when burned, it produces $SO_2$ fumes that are toxic to most organisms, including vermin hiding in the walls and under the floors of houses. Hence references to sulfur are common in ancient literature, frequently in the context of religious purification. In fact, the association of sulfur with the divine was so pervasive that the prefixes thio- (meaning “sulfur”) and theo- (meaning “god”) have the same root in ancient Greek. Though used primarily in the production of sulfuric acid, sulfur is also used to manufacture gunpowder and as a cross-linking agent for rubber, which enables rubber to hold its shape but retain its flexibility.

> *Group 16 is the first group in the p block with no stable metallic elements.*

Oxygen was not discovered until 1771, when the Swedish pharmacist Carl Wilhelm Scheele found that heating compounds such as $KNO_3$, $Ag_2CO_3$, and HgO produced a colorless, odorless gas that supported combustion better than air. The results were not published immediately, however, so Scheele’s work remained unknown until 1777. Unfortunately, this was nearly two years after a paper by the English chemist Joseph Priestley had been published, describing the isolation of the same gas by using a magnifying glass to focus the sun’s rays on a sample of HgO. Oxygen is used primarily in the steel industry during the conversion of crude iron to steel using the Bessemer process. Another important industrial use of oxygen is in the production of $TiO_2$, which is commonly used as a white pigment in paints, paper, and plastics.



Figure 21.4.1: A crystalline sulfur deposit. This sulfur deposit is located around a volcanic vent in Kilauea Crater, Hawaii.

Tellurium was discovered accidentally in 1782 by the Austrian chemist Franz Joseph Müller von Reichenstein, the chief surveyor of mines in Transylvania who was also responsible for the analysis of ore samples. The silvery-white metal had the same density as antimony but very different properties. Because it was difficult to analyze, Müller called it metallum problematicum (meaning “difficult metal”). The name tellurium (from the Latin tellus, meaning “earth”) was coined by another Austrian chemist, Martin Klaproth, who demonstrated in 1798 that Müller’s “difficult metal” was actually a new element. Tellurium is used to color glass and ceramics, in the manufacture of blasting caps, and in thermoelectric devices.

**Jöns Jakob Berzelius (1779–1848)**

Berzelius was born into a well-educated Swedish family, but both parents died when he was young. He studied medicine at the University of Uppsala, where his experiments with electroshock therapy caused his interests to turn to electrochemistry. Berzelius devised the system of chemical notation that we use today. In addition, he discovered six elements (cerium, thorium, selenium, silicon, titanium, and zirconium).

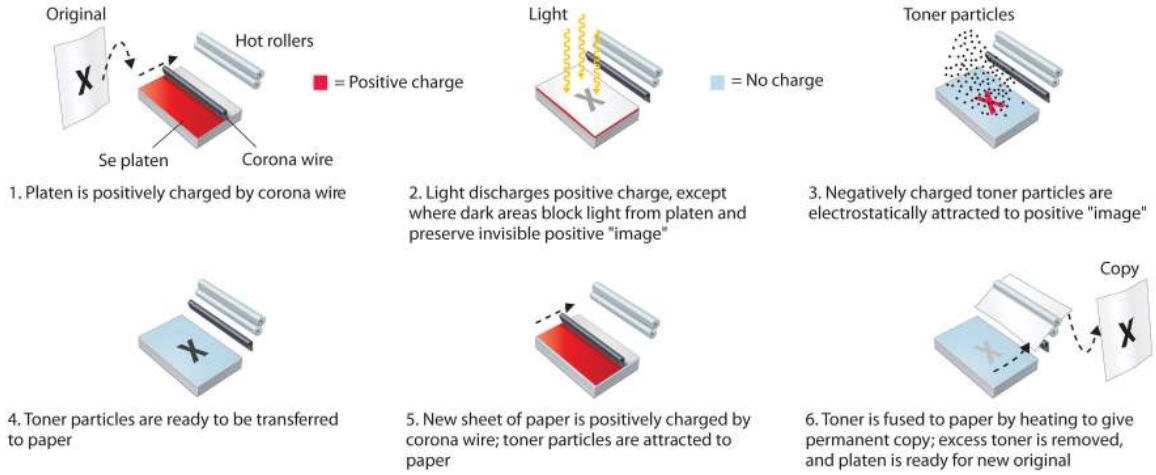



Figure 21.4.1: The Chemistry of Photocopying. Because amorphous selenium is a photosensitive semiconductor, exposing an electrostatically charged Se film to light causes the positive charge on the film to be discharged in all areas that are white in the original. Dark areas in the original block the light and generate an invisible, positively charged image. To produce an image on paper, negatively charged toner particles are attracted to the positive image, transferred to a negatively charged sheet of blank paper, and fused with the paper at high temperature to give a permanent image.

The heaviest chalcogen, polonium, was isolated after an extraordinary effort by Marie Curie. Although she was never able to obtain macroscopic quantities of the element, which she named for her native country of Poland, she demonstrated that its chemistry required it to be assigned to group 16. Marie Curie was awarded a second Nobel Prize in Chemistry in 1911 for the discovery of radium and polonium.

## Preparation and General Properties of the Group 16 Elements

Oxygen is by far the most abundant element in Earth's crust and in the hydrosphere (about 44% and 86% by mass, respectively). The same process that is used to obtain nitrogen from the atmosphere produces pure oxygen. Oxygen can also be obtained by the electrolysis of water, the decomposition of alkali metal or alkaline earth peroxides or superoxides, or the thermal decomposition of simple inorganic salts, such as potassium chlorate in the presence of a catalytic amount of $MnO_2$:

$$2KClO_3(s) \overset{\underset{\Delta}{MnO_2(s)}}{\rightleftharpoons} 2KCl(s) + 3O_2(g) \tag{21.4.1}$$

Unlike oxygen, sulfur is not very abundant, but it is found as elemental sulfur in rock formations overlying salt domes, which often accompany petroleum deposits (Figure 21.4.1). Sulfur is also recovered from $H_2S$ and organosulfur compounds in crude oil and coal and from metal sulfide ores such as pyrite ($FeS_2$).



Pyrite ($FeS_2$). Because of its lustrous golden yellow cubic crystals, $FeS_2$ is sometimes mistaken for gold, giving rise to its common name "fool's gold." Real gold, however, is much denser than $FeS_2$, and gold is soft and malleable rather than hard and brittle.

Because selenium and tellurium are chemically similar to sulfur, they are usually found as minor contaminants in metal sulfide ores and are typically recovered as by-products. Even so, they are as abundant in Earth's crust as silver, palladium, and gold. One of the best sources of selenium and tellurium is the "slime" deposited during the electrolytic purification of copper. Both of these elements are notorious for the vile odors of many of their compounds. For example, when the body absorbs even trace amounts of tellurium, dimethyltellurium [$(CH_3)_2Te$] is produced and slowly released in the breath and perspiration, resulting in an intense garlic-like smell that is commonly called "tellurium breath."

With their $ns^2np^4$ electron configurations, the chalcogens are two electrons short of a filled valence shell. Thus in reactions with metals, they tend to acquire two additional electrons to form compounds in the −2 oxidation state. This tendency is greatest for oxygen, the chalcogen with the highest electronegativity. The heavier, less electronegative chalcogens can lose either four np electrons or four np and two ns electrons to form compounds in the +4 and +6 oxidation state, respectively, as shown in Table Figure 21.4.1. As with the other groups, the lightest member in the group, in this case oxygen, differs greatly from the others in size, ionization energy, electronegativity, and electron affinity, so its chemistry is unique. Also as in the other groups, the second and third members (sulfur and selenium) have similar properties because of shielding effects. Only polonium is metallic, forming either the hydrated $Po^{2+}$ or $Po^{4+}$ ion in aqueous solution, depending on conditions.

Table 21.4.1: Selected Properties of the Group 16 Elements

| Property | Oxygen | Sulfur | Selenium | Tellurium | Polonium |
|---|---|---|---|---|---|
| atomic mass (amu) | 16.00 | 32.07 | 78.96 | 127.60 | 209 |
| atomic number | 8 | 16 | 34 | 52 | 84 |
| atomic radius (pm) | 48 | 88 | 103 | 123 | 135 |
| atomic symbol | O | S | Se | Te | Po |
| density ($g/cm^3$) at 25°C | 1.31 (g/L) | 2.07 | 4.81 | 6.24 | 9.20 |
| electron affinity (kJ/mol) | −141 | −200 | −195 | −190 | −180 |
| electronegativity | 3.4 | 2.6 | 2.6 | 2.1 | 2.0 |
| first ionization energy (kJ/mol) | 1314 | 1000 | 941 | 869 | 812 |
| ionic radius (pm)† | 140 (−2) | 184 (−2), 29 (+6) | 198 (−2), 42 (+6) | 221 (−2), 56 (+6) | 230 (−2), 97 (+4) |
| melting point/boiling point (°C) | −219/−183 | 115/445 | 221/685 | 450/988 | 254/962 |
| normal oxidation state(s) | −2 | +6, +4, −2 | +6, +4, −2 | +6, +4, −2 | +2 (+4) |
| product of reaction with $H_2$ | $H_2O$ | $H_2S$ | $H_2Se$ | none | none |
| product of reaction with $N_2$ | NO, $NO_2$ | none | none | none | none |
| product of reaction with $O_2$ | — | $SO_2$ | $SeO_2$ | $TeO_2$ | $PoO_2$ |
| product of reaction with $X_2$ | $O_2F_2$ | $SF_6$, $S_2Cl_2$, $S_2Br_2$ | $SeF_6$, $SeX_4$ | $TeF_6$, $TeX_4$ | $PoF_4$, $PoCl_2$, $PoBr_2$ |
| standard reduction potential (E°, V) ($E^0$ → $H_2E$ in acidic solution) | +1.23 | +0.14 | −0.40 | −0.79 | −1.00 |
| type of oxide | — | acidic | acidic | amphoteric | basic |
| valence electron configuration* | $2s^22p^4$ | $3s^23p^4$ | $4s^24p^4$ | $5s^25p^4$ | $6s^26p^4$ |

*The configuration shown does not include filled d and f subshells.

†The values cited for the hexacations are for six-coordinate ions and are only estimated values.

## Reactions and Compounds of Oxygen

As in groups 14 and 15, the lightest group 16 member has the greatest tendency to form multiple bonds. Thus elemental oxygen is found in nature as a diatomic gas that contains a net double bond: O=O. As with nitrogen, electrostatic repulsion between lone pairs of electrons on adjacent atoms prevents oxygen from forming stable catenated compounds. In fact, except for $O_2$, all compounds that contain O–O bonds are potentially explosive. Ozone, peroxides, and superoxides are all potentially dangerous in pure form.

Ozone ($O_3$), one of the most powerful oxidants known, is used to purify drinking water because it does not produce the characteristic taste associated with chlorinated water. Hydrogen peroxide ($H_2O_2$) is so thermodynamically unstable that it has a tendency to undergo explosive decomposition when impure:

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)} \qquad \Delta G^o = -119\ kJ/mol \tag{21.4.2}$$

> *As in groups 14 and 15, the lightest element in group 16 has the greatest tendency to form multiple bonds.*

Despite the strength of the O=O bond ($D_{O_2}$ = 494 kJ/mol), $O_2$ is extremely reactive, reacting directly with nearly all other elements except the noble gases. Some properties of $O_2$ and related species, such as the peroxide and superoxide ions, are in Table 21.4.2. With few exceptions, the chemistry of oxygen is restricted to negative oxidation states because of its high electronegativity (χ = 3.4). Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Oxygen is second only to fluorine in its ability to stabilize high oxidation states of metals in both ionic and covalent compounds. For example, AgO is a stable solid that contains silver in the unusual Ag(II) state, whereas $OsO_4$ is a volatile solid that contains Os(VIII). Because oxygen is so electronegative, the O–H bond is highly polar, creating a large bond dipole moment that makes hydrogen bonding much more important for compounds of oxygen than for similar compounds of the other chalcogens.

Table 21.4.2: Some Properties of $O_2$ and Related Diatomic Species

| Species | Bond Order | Number of Unpaired $e^-$ | O–O Distance (pm)* |
|---|---|---|---|
| $O_2^+$ | 2.5 | 1 | 112 |
| $O_2$ | 2 | 2 | 121 |
| $O_2^-$ | 1.5 | 1 | 133 |
| $O_2^{2-}$ | 1 | 0 | 149 |

*Source of data: Lauri Vaska, “Dioxygen-Metal Complexes: Toward a Unified View,” Accounts of Chemical Research 9 (1976): 175.

Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements that lie on or near the diagonal band of semimetals are generally amphoteric. A few oxides, such as CO and $PbO_2$, are neutral and do not react with water, aqueous acid, or aqueous base. Nonmetal oxides are typically covalent compounds in which the bonds between oxygen and the nonmetal are polarized ($E^{\delta+}$–$O^{\delta-}$). Consequently, a lone pair of electrons on a water molecule can attack the partially positively charged E atom to eventually form an oxoacid. An example is reacting sulfur trioxide with water to form sulfuric acid:

$$H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(aq)} \tag{21.4.3}$$

The oxides of the semimetals and of elements such as Al that lie near the metal/nonmetal dividing line are amphoteric, as we expect:

$$Al_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)} \tag{21.4.4}$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} \tag{21.4.5}$$

> *Oxides of metals tend to be basic, oxides of nonmetals tend to be acidic, and oxides of elements in or near the diagonal band of semimetals are generally amphoteric.*

**Example 21.4.1**

For each reaction, explain why the given products form.

a. $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4^-(aq)$
b. $3H_2O_2(aq) + 2MnO_4^-(aq) + 2H^+(aq) \rightarrow 3O_2(g) + 2MnO_2(s) + 4H_2O(l)$
c. $KNO_3(s) \xrightarrow{\Delta} KNO(s) + O_2(g)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

**Solution**

a. Gallium is a metal. We expect the oxides of metallic elements to be basic and therefore not to react with aqueous base. A close look at the periodic table, however, shows that gallium is close to the diagonal line of semimetals. Moreover, aluminum, the element immediately above gallium in group 13, is amphoteric. Consequently, we predict that gallium will behave like aluminum (Equation 21.4.5).

b. Hydrogen peroxide is an oxidant that can accept two electrons per molecule to give two molecules of water. With a strong oxidant, however, $H_2O_2$ can also act as a reductant, losing two electrons (and two protons) to produce $O_2$. Because the other reactant is permanganate, which is a potent oxidant, the only possible reaction is a redox reaction in which permanganate is the oxidant and hydrogen peroxide is the reductant. Recall that reducing permanganate often gives $MnO_2$, an insoluble brown solid. Reducing $MnO_4^-$ to $MnO_2$ is a three-electron reduction, whereas the oxidation of $H_2O_2$ to $O_2$ is a two-electron oxidation.

c. This is a thermal decomposition reaction. Because $KNO_3$ contains nitrogen in its highest oxidation state (+5) and oxygen in its lowest oxidation state (−2), a redox reaction is likely. Oxidation of the oxygen in nitrate to atomic oxygen is a two-electron process per oxygen atom. Nitrogen is likely to accept two electrons because oxoanions of nitrogen are known only in the +5 ($NO_3^-$) and +3 ($NO_2^-$) oxidation states.

**? Exercise 21.4.2**

Predict the product(s) of each reaction and write a balanced chemical equation for each reaction.

a. $SiO_2(s) + H^+(aq) \rightarrow$
b. $NO(g) + O_2(g) \rightarrow$
c. $SO_3(g) + H_2O(l) \rightarrow$
d. $H_2O_2(aq) + I^-(aq) \rightarrow$

**Answer**

a. $SiO_2(s) + H^+(aq) \rightarrow$ no reaction
b. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
c. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
d. $H_2O_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2OH^-(aq)$

## Reactions and Compounds of the Heavier Chalcogens

Because most of the heavier chalcogens (group 16) and pnicogens (group 15) are nonmetals, they often form similar compounds. For example, both third-period elements of these groups (phosphorus and sulfur) form catenated compounds and form multiple allotropes. Consistent with periodic trends, the tendency to catenate decreases as we go down the column.

Sulfur and selenium both form a fairly extensive series of catenated species. For example, elemental sulfur forms $S_8$ rings packed together in a complex “crankshaft” arrangement (Figure 21.4.2), and molten sulfur contains long chains of sulfur atoms connected by S–S bonds. Moreover, both sulfur and selenium form polysulfides ($S_n^{2-}$) and polyselenides ($Se_n^{2-}$), with $n \le 6$. The only stable allotrope of tellurium is a silvery white substance whose properties and structure are similar to those of one of the selenium allotropes. Polonium, in contrast, shows no tendency to form catenated compounds. The striking decrease in structural complexity from sulfur to polonium is consistent with the decrease in the strength of single bonds and the increase in metallic character as we go down the group.

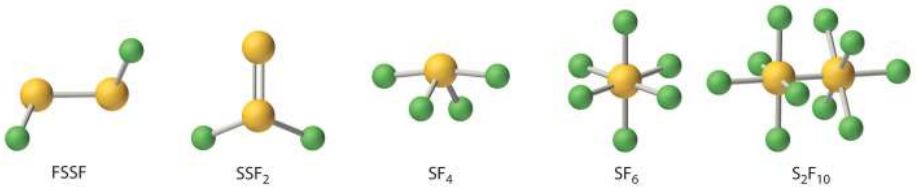



Figure 21.4.2: The Structures of the Known Fluorides of Sulfur. Five stable sulfur fluorides are known, containing sulfur in oxidation states ranging from +1 to +6. All are volatile molecular compounds that vary tremendously in stability and toxicity. Although both $SF_6$ and $S_2F_{10}$ are very stable, $S_2F_{10}$ is toxic and $SF_6$ is not. The other three are highly reactive substances.

As in group 15, the reactivity of elements in group 16 decreases from lightest to heaviest. For example, selenium and tellurium react with most elements but not as readily as sulfur does. As expected for nonmetals, sulfur, selenium, and tellurium do not react with water, aqueous acid, or aqueous base, but all dissolve in strongly oxidizing acids such as $HNO_3$ to form oxoacids such as $H_2SO_4$. In contrast to the other chalcogens, polonium behaves like a metal, dissolving in dilute HCl to form solutions that contain the $Po^{2+}$ ion.

> *Just as with the other groups, the tendency to catenate, the strength of single bonds, and reactivity decrease down the group.*

Fluorine reacts directly with all chalcogens except oxygen to produce the hexafluorides ($YF_6$), which are extraordinarily stable and unreactive compounds. Four additional stable fluorides of sulfur are known; thus sulfur oxidation states range from +1 to +6 (Figure 21.4.2). In contrast, only four fluorides of selenium ($SeF_6$, $SeF_4$, FSeSeF, and $SeSeF_2$) and only three of tellurium ($TeF_4$, $TeF_6$, and $Te_2F_{10}$) are known.

Direct reaction of the heavier chalcogens with oxygen at elevated temperatures gives the dioxides ($YO_2$), which exhibit a dramatic range of structures and properties. The dioxides become increasingly metallic in character down the group, as expected, and the coordination number of the chalcogen steadily increases. Thus $SO_2$ is a gas that contains V-shaped molecules (as predicted by the valence-shell electron-pair repulsion model), $SeO_2$ is a white solid with an infinite chain structure (each Se is three coordinate), $TeO_2$ is a light yellow solid with a network structure in which each Te atom is four coordinate, and $PoO_2$ is a yellow ionic solid in which each $Po^{4+}$ ion is eight coordinate.

The dioxides of sulfur, selenium, and tellurium react with water to produce the weak, diprotic oxoacids ($H_2YO_3$—sulfurous, selenous, and tellurous acid, respectively). Both sulfuric acid and selenic acid ($H_2SeO_4$) are strong acids, but telluric acid [$Te(OH)_6$] is quite different. Because tellurium is larger than either sulfur or selenium, it forms weaker π bonds to oxygen. As a result, the most stable structure for telluric acid is $Te(OH)_6$, with six Te–OH bonds rather than Te=O bonds. Telluric acid therefore behaves like a weak triprotic acid in aqueous solution, successively losing the hydrogen atoms bound to three of the oxygen atoms. As expected for compounds that contain elements in their highest accessible oxidation state (+6 in this case), sulfuric, selenic, and telluric acids are oxidants. Because the stability of the highest oxidation state decreases with increasing atomic number, telluric acid is a stronger oxidant than sulfuric acid.

> *The stability of the highest oxidation state of the chalcogens decreases down the column.*

Sulfur and, to a lesser extent, selenium react with carbon to form an extensive series of compounds that are structurally similar to their oxygen analogues. For example, $CS_2$ and $CSe_2$ are both volatile liquids that contain C=S or C=Se bonds and have the same linear structure as $CO_2$. Because these double bonds are significantly weaker than the C=O bond, however, $CS_2$, $CSe_2$, and related compounds are less stable and more reactive than their oxygen analogues. The chalcogens also react directly with nearly all metals to form compounds with a wide range of stoichiometries and a variety of structures. Metal chalcogenides can contain either the simple chalcogenide ion ($Y^{2-}$), as in $Na_2S$ and FeS, or polychalcogenide ions ($Y_n^{2-}$), as in $FeS_2$ and $Na_2S_5$.

> *The dioxides of the group 16 elements become increasingly basic, and the coordination number of the chalcogen steadily increases down the group.*

Ionic chalcogenides like $Na_2S$ react with aqueous acid to produce binary hydrides such as hydrogen sulfide ($H_2S$). Because the strength of the Y–H bond decreases with increasing atomic radius, the stability of the binary hydrides decreases rapidly down the group. It is perhaps surprising that hydrogen sulfide, with its familiar rotten-egg smell, is much more toxic than hydrogen cyanide

(HCN), the gas used to execute prisoners in the "gas chamber." Hydrogen sulfide at relatively low concentrations deadens the olfactory receptors in the nose, which allows it to reach toxic levels without detection and makes it especially dangerous.

### Example 21.4.2

For each reaction, explain why the given product forms or no reaction occurs.

a. $SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$
b. $SF_6(g) + H_2O(l) \rightarrow$ no reaction
c. $2Se(s) + Cl_2(g) \rightarrow Se_2Cl_2(l)$

**Given:** balanced chemical equations

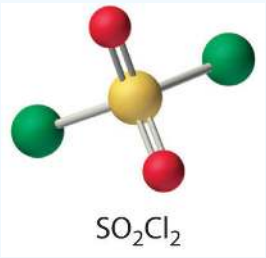
**Asked for:** why the given products (or no products) form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form or why no reaction occurs.

**Solution**

a. One of the reactants ($Cl_2$) is an oxidant. If the other reactant can be oxidized, then a redox reaction is likely. Sulfur dioxide contains sulfur in the +4 oxidation state, which is 2 less than its maximum oxidation state. Sulfur dioxide is also known to be a mild reducing agent in aqueous solution, producing sulfuric acid as the oxidation product. Hence a redox reaction is probable. The simplest reaction is the formation of $SO_2Cl_2$ (sulfuryl chloride), which is a tetrahedral species with two S–Cl and two S=O bonds.




b. Sulfur hexafluoride is a nonmetallic halide. Such compounds normally react vigorously with water to produce an oxoacid of the nonmetal and the corresponding hydrohalic acid. In this case, however, we have a highly stable species, presumably because all of sulfur's available orbitals are bonding orbitals. Thus $SF_6$ is not likely to react with water.
c. Here we have the reaction of a chalcogen with a halogen. The halogen is a good oxidant, so we can anticipate that a redox reaction will occur. Only fluorine is capable of oxidizing the chalcogens to a +6 oxidation state, so we must decide between $SeCl_4$ and $Se_2Cl_2$ as the product. The stoichiometry of the reaction determines which of the two is obtained: $SeCl_4$ or $Se_2Cl_2$.

### Exercise 21.4.2

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $Te(s) + Na(s) \xrightarrow{\Delta}$
b. $SF_4(g) + H_2O(l) \rightarrow$
c. $CH_3SeSeCH_3(soln) + K(s) \rightarrow$
d. $Li_2Se(s) + H^+(aq) \rightarrow$

**Answer**

a. $Te(s) + 2Na(s) \rightarrow Na_2Te(s)$
b. $SF_4(g) + 3H_2O(l) \rightarrow H_2SO_3(aq) + 4HF(aq)$
c. $CH_3SeSeCH_3(soln) + 2K(s) \rightarrow 2KCH_3Se(soln)$

d. $Li_2Se(s) + 2H^+(aq) \rightarrow H_2Se(g) + 2Li^+(aq)$

## Summary

The chalcogens have no stable metallic elements. The tendency to catenate, the strength of single bonds, and the reactivity all decrease moving down the group. Because the electronegativity of the chalcogens decreases down the group, so does their tendency to acquire two electrons to form compounds in the −2 oxidation state. The lightest member, oxygen, has the greatest tendency to form multiple bonds with other elements. It does not form stable catenated compounds, however, due to repulsions between lone pairs of electrons on adjacent atoms. Because of its high electronegativity, the chemistry of oxygen is generally restricted to compounds in which it has a negative oxidation state, and its bonds to other elements tend to be highly polar. Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements along the dividing line between metals and nonmetals are amphoteric. The reactivity, the strength of multiple bonds to oxygen, and the tendency to form catenated compounds all decrease down the group, whereas the maximum coordination numbers increase. Because Te=O bonds are comparatively weak, the most stable oxoacid of tellurium contains six Te–OH bonds. The stability of the highest oxidation state (+6) decreases down the group. Double bonds between S or Se and second-row atoms are weaker than the analogous C=O bonds because of reduced orbital overlap. The stability of the binary hydrides decreases down the group.

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# 21.5: The Elements of Group 17 (The Halogens)

**Learning Objectives**

- To understand the periodic trends and reactivity of the group 17 elements: the halogens.

Because the halogens are highly reactive, none is found in nature as the free element. Hydrochloric acid, which is a component of aqua regia (a mixture of HCl and $HNO_3$ that dissolves gold), and the mineral fluorspar ($CaF_2$) were well known to alchemists, who used them in their quest for gold. Despite their presence in familiar substances, none of the halogens was even recognized as an element until the 19th century.

> *Because the halogens are highly reactive, none is found in nature as the free element.*

Chlorine was the first halogen to be obtained in pure form. In 1774, Carl Wilhelm Scheele (the codiscoverer of oxygen) produced chlorine by reacting hydrochloric acid with manganese dioxide. Scheele was convinced, however, that the pale green gas he collected over water was a compound of oxygen and hydrochloric acid. In 1811, Scheele's "compound" was identified as a new element, named from the Greek chloros, meaning "yellowish green" (the same stem as in chlorophyll, the green pigment in plants). That same year, a French industrial chemist, Bernard Courtois, accidentally added too much sulfuric acid to the residue obtained from burned seaweed. A deep purple vapor was released, which had a biting aroma similar to that of Scheele's "compound." The purple substance was identified as a new element, named iodine from the Greek iodes, meaning "violet." Bromine was discovered soon after by a young French chemist, Antoine Jérôme Balard, who isolated a deep red liquid with a strong chlorine-like odor from brine from the salt marshes near Montpellier in southern France. Because many of its properties were intermediate between those of chlorine and iodine, Balard initially thought he had isolated a compound of the two (perhaps ICl). He soon realized, however, that he had discovered a new element, which he named bromine from the Greek bromos, meaning "stench." Currently, organic chlorine compounds, such as PVC (polyvinylchloride), consume about 70% of the $Cl_2$ produced annually; organobromine compounds are used in much smaller quantities, primarily as fire retardants.



A crystal of the mineral fluorite ($CaF_2$). The purple color of some fluorite crystals is due to small inclusions of highly oxidizing impurities, which generate detectable amounts of ozone when the crystals are crushed.

Because of the unique properties of its compounds, fluorine was believed to exist long before it was actually isolated. The mineral fluorspar (now called fluorite [$CaF_2$]) had been used since the 16th century as a "flux," a low-melting-point substance that could dissolve other minerals and ores. In 1670, a German glass cutter discovered that heating fluorspar with strong acid produced a solution that could etch glass. The solution was later recognized to contain the acid of a new element, which was named fluorine in 1812. Elemental fluorine proved to be very difficult to isolate, however, because both HF and $F_2$ are extraordinarily reactive and toxic. After being poisoned three times while trying to isolate the element, the French chemist Henri Moissan succeeded in 1886 in electrolyzing a sample of KF in anhydrous HF to produce a pale green gas (Figure 21.5.1). For this achievement, among others, Moissan narrowly defeated Mendeleev for the Nobel Prize in Chemistry in 1906. Large amounts of fluorine are now consumed in the production of cryolite ($Na_3AlF_6$), a key intermediate in the production of aluminum metal. Fluorine is also found in teeth as fluoroapatite [$Ca_5(PO_4)_3F$], which is formed by reacting hydroxyapatite [$Ca_5(PO_4)_3OH$] in tooth enamel with fluoride ions in toothpastes, rinses, and drinking water.



Figure 21.5.1 Isolation of Elemental Fluorine. The French chemist Henri Moissan was the first person to isolate elemental fluorine. A reproduction of the U-shaped electrolysis cell with which Moissan first isolated elemental fluorine in 1866 is shown with samples of cryolite (left) and fluorspar (right). Fluorspar is the raw material from which anhydrous hydrofluoric acid (HF) is prepared. Cryolite is a rare mineral that contains the fluoride ion.

The heaviest halogen is astatine (At), which is continuously produced by natural radioactive decay. All its isotopes are highly radioactive, and the most stable has a half-life of only about 8 h. Consequently, astatine is the least abundant naturally occurring element on Earth, with less than 30 g estimated to be present in Earth's crust at any one time.

## Preparation and General Properties of the Group 17 Elements

All the halogens except iodine are found in nature as salts of the halide ions ($X^-$), so the methods used for preparing $F_2$, $Cl_2$, and $Br_2$ all involve oxidizing the halide. Reacting $CaF_2$ with concentrated sulfuric acid produces gaseous hydrogen fluoride:

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF_{(g)} \tag{21.5.1}$$

Fluorine is produced by the electrolysis of a 1:1 mixture of HF and $K^+HF_2^-$ at 60–300°C in an apparatus made of Monel, a highly corrosion-resistant nickel–copper alloy:

$$KHF_2 \cdot HF(l) \xrightarrow{electrolysis} F_2(g) + H_2(g) \tag{21.5.2}$$

Fluorine is one of the most powerful oxidants known, and both $F_2$ and HF are highly corrosive. Consequently, the production, storage, shipping, and handling of these gases pose major technical challenges.

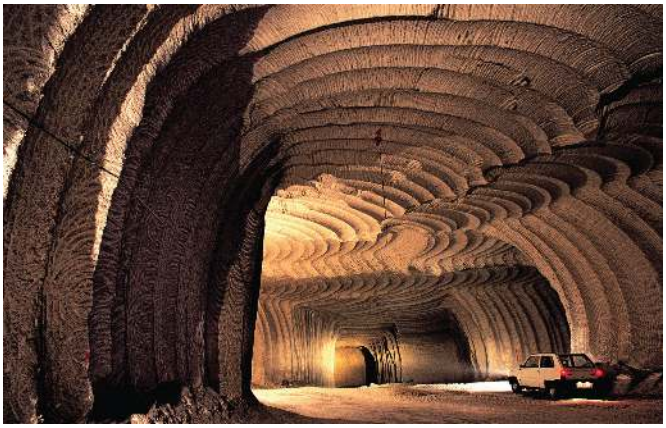


Figure 21.5.2: A Subterranean Salt Mine. Subterranean deposits of rock salt are located worldwide, such as this one at Petralia in Sicily.

Although chlorine is significantly less abundant than fluorine, elemental chlorine is produced on an enormous scale. Fortunately, large subterranean deposits of rock salt (NaCl) are found around the world (Figure 21.5.2), and seawater consists of about 2% NaCl by mass, providing an almost inexhaustible reserve. Inland salt lakes such as the Dead Sea and the Great Salt Lake are even richer sources, containing about 23% and 8% NaCl by mass, respectively. Chlorine is prepared industrially by the chloralkali process, which uses the following reaction:

$$2NaCl_{(aq)} + 2H_2O_{(l)} \xrightarrow{electrolysis} 2NaOH(aq) + Cl_{2(g)} + H_{2(g)} \tag{21.5.3}$$

Bromine is much less abundant than fluorine or chlorine, but it is easily recovered from seawater, which contains about 65 mg of $Br^-$ per liter. Salt lakes and underground brines are even richer sources; for example, the Dead Sea contains 4 g of $Br^-$ per liter.

Iodine is the least abundant of the nonradioactive halogens, and it is a relatively rare element. Because of its low electronegativity, iodine tends to occur in nature in an oxidized form. Hence most commercially important deposits of iodine, such as those in the Chilean desert, are iodate salts such as $Ca(IO_3)_2$. The production of iodine from such deposits therefore requires reduction rather than oxidation. The process is typically carried out in two steps: reduction of iodate to iodide with sodium hydrogen sulfite, followed by reaction of iodide with additional iodate:

$$2IO^-_{3(aq)} + 6HSO^-_{3(aq)} \rightarrow 2I^-_{(aq)} + 6SO^2 -_{4(aq)} + 6H^+_{(aq)} \tag{21.5.4}$$

$$5I^-_{(aq)} + IO^-_{3(aq)} + 6H^+_{(aq)} \rightarrow 3I_{2(s)} + 3H_2O_{(l)} \tag{21.5.5}$$

Because the halogens all have $ns^2np^5$ electron configurations, their chemistry is dominated by a tendency to accept an additional electron to form the closed-shell ion ($X^-$). Only the electron affinity and the bond dissociation energy of fluorine differ significantly from the expected periodic trends shown in Table 21.5.1. Electron–electron repulsion is important in fluorine because of its small atomic volume, making the electron affinity of fluorine less than that of chlorine. Similarly, repulsions between electron pairs on adjacent atoms are responsible for the unexpectedly low F–F bond dissociation energy. (As discussed earlier, this effect is also responsible for the weakness of O–O, N–N, and N–O bonds.)

> *Electrostatic repulsions between lone pairs of electrons on adjacent atoms cause single bonds between N, O, and F to be weaker than expected.*

Table 21.5.1: Selected Properties of the Group 17 Elements

| Property | Fluorine | Chlorine | Bromine | Iodine | Astatine |
|---|---|---|---|---|---|
| atomic symbol | F | Cl | Br | I | At |
| atomic number | 9 | 17 | 35 | 53 | 85 |
| atomic mass (amu) | 19.00 | 35.45 | 79.90 | 126.90 | 210 |
| valence electron configuration* | $2s^2 2p^5$ | $3s^2 3p^5$ | $4s^2 4p^5$ | $5s^2 5p^5$ | $6s^2 6p^5$ |
| melting point/boiling point (°C) | −220/−188 | −102/−34.0 | −7.2/58.8 | 114/184 | 302/— |
| density ($g/cm^3$) at 25°C | 1.55 (g/L) | 2.90 (g/L) | 3.10 | 4.93 | — |
| atomic radius (pm) | 42 | 79 | 94 | 115 | 127 |
| first ionization energy (kJ/mol) | 1681 | 1251 | 1140 | 1008 | 926 |
| normal oxidation state(s) | −1 | −1 (+1, +3, +5, +7) | −1 (+1, +3, +5, +7) | −1 (+1, +3, +5, +7) | −1, +1 |
| ionic radius (pm)† | 133 | 181 | 196 | 220 | — |
| electron affinity (kJ/mol) | −328 | −349 | −325 | −295 | −270 |
| electronegativity | 4.0 | 3.2 | 3.0 | 2.7 | 2.2 |
| standard reduction potential (E°, V) ($X_2 \rightarrow X^-$ in basic solution) | +2.87 | +1.36 | +1.07 | +0.54 | +0.30 |
| dissociation energy of $X_2(g)$ (kJ/mol) | 158.8 | 243.6 | 192.8 | 151.1 | ~80 |
| product of reaction with $O_2$ | $O_2F_2$ | none | none | none | none |
| type of oxide | acidic | acidic | acidic | acidic | acidic |
| product of reaction with $N_2$ | none | none | none | none | none |
| product of reaction with $H_2$ | HF | HCl | HBr | HI | HAt |

*The configuration shown does not include filled d and f subshells. †The values cited are for the six-coordinate anion ($X^-$).

Because it is the most electronegative element in the periodic table, fluorine forms compounds in only the −1 oxidation state. Notice, however, that all the halogens except astatine have electronegativities greater than 2.5, making their chemistry exclusively that of nonmetals. The halogens all have relatively high ionization energies, but the energy required to remove electrons decreases substantially as we go down the column. Hence the heavier halogens also form compounds in positive oxidation states (+1, +3, +5, and +7), derived by the formal loss of ns and np electrons.

> *Because ionization energies decrease down the group, the heavier halogens form compounds in positive oxidation states (+1, +3, +5, and +7).*

## Reactions and Compounds of the Halogens

Fluorine is the most reactive element in the periodic table, forming compounds with every other element except helium, neon, and argon. The reactions of fluorine with most other elements range from vigorous to explosive; only $O_2$, $N_2$, and Kr react slowly. There are three reasons for the high reactivity of fluorine:

1. Because fluorine is so electronegative, it is able to remove or at least share the valence electrons of virtually any other element.
2. Because of its small size, fluorine tends to form very strong bonds with other elements, making its compounds thermodynamically stable.
3. The F–F bond is weak due to repulsion between lone pairs of electrons on adjacent atoms, reducing both the thermodynamic and kinetic barriers to reaction.

With highly electropositive elements, fluorine forms ionic compounds that contain the closed-shell $F^-$ ion. In contrast, with less electropositive elements (or with metals in very high oxidation states), fluorine forms covalent compounds that contain terminal F atoms, such as $SF_6$. Because of its high electronegativity and $2s^22p^5$ valence electron configuration, fluorine normally participates in only one electron-pair bond. Only a very strong Lewis acid, such as $AlF_3$, can share a lone pair of electrons with a fluoride ion, forming $AlF_6^{3-}$.

> *Oxidative strength decreases down group 17.*

The halogens ($X_2$) react with metals (M) according to the general equation

$$M_{(s,l)} + nX_{2(s,l,g)} \rightarrow MX_{n(s,l)} \tag{21.5.6}$$

For elements that exhibit multiple oxidation states fluorine tends to produce the highest possible oxidation state and iodine the lowest. For example, vanadium reacts with the halogens to give $VF_5$, $VCl_4$, $VBr_4$, and $VI_3$.

Metal halides in the +1 or +2 oxidation state, such as $CaF_2$, are typically ionic halides, which have high melting points and are often soluble in water. As the oxidation state of the metal increases, so does the covalent character of the halide due to polarization of the M–X bond. With its high electronegativity, fluoride is the least polarizable, and iodide, with the lowest electronegativity, is the most polarizable of the halogens. Halides of small trivalent metal ions such as $Al^{3+}$ tend to be relatively covalent. For example, $AlBr_3$ is a volatile solid that contains bromide-bridged $Al_2Br_6$ molecules. In contrast, the halides of larger trivalent metals, such as the lanthanides, are essentially ionic. For example, indium tribromide ($InBr_3$) and lanthanide tribromide ($LnBr_3$) are all high-melting-point solids that are quite soluble in water.

> *As the oxidation state of the metal increases, the covalent character of the corresponding metal halides also increases due to polarization of the M–X bond.*

All halogens react vigorously with hydrogen to give the hydrogen halides (HX). Because the H–F bond in HF is highly polarized ($H^{\delta+}$–$F^{\delta-}$), liquid HF has extensive hydrogen bonds, giving it an unusually high boiling point and a high dielectric constant. As a result, liquid HF is a polar solvent that is similar in some ways to water and liquid ammonia; after a reaction, the products can be recovered simply by evaporating the HF solvent. (Hydrogen fluoride must be handled with extreme caution, however, because contact of HF with skin causes extraordinarily painful burns that are slow to heal.) Because fluoride has a high affinity for silicon, aqueous hydrofluoric acid is used to etch glass, dissolving $SiO_2$ to give solutions of the stable $SiF_6^{2-}$ ion.



***Glass etched with hydrogen flouride.*** *© Thinkstock*

Except for fluorine, all the halogens react with water in a disproportionation reaction, where X is Cl, Br, or I:

$$X_{2(g,l,s)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + X^-_{(aq)} + HOX_{(aq)} \tag{21.5.7}$$

The most stable oxoacids are the perhalic acids, which contain the halogens in their highest oxidation state (+7). The acid strengths of the oxoacids of the halogens increase with increasing oxidation state, whereas their stability and acid strength decrease down the group. Thus perchloric acid ($HOClO_3$, usually written as $HClO_4$) is a more potent acid and stronger oxidant than perbromic acid. Although all the oxoacids are strong oxidants, some, such as $HClO_4$, react rather slowly at low temperatures. Consequently, mixtures of the halogen oxoacids or oxoanions with organic compounds are potentially explosive if they are heated or even agitated mechanically to initiate the reaction. Because of the danger of explosions, oxoacids and oxoanions of the halogens should never be allowed to come into contact with organic compounds.

> *Both the acid strength and the oxidizing power of the halogen oxoacids decrease down the group.*

The halogens react with one another to produce interhalogen compounds, such as $ICl_3$, $BrF_5$, and $IF_7$. In all cases, the heavier halogen, which has the lower electronegativity, is the central atom. The maximum oxidation state and the number of terminal halogens increase smoothly as the ionization energy of the central halogen decreases and the electronegativity of the terminal halogen increases. Thus depending on conditions, iodine reacts with the other halogens to form $IF_n$ (n = 1–7), ICl or $ICl_3$, or IBr, whereas bromine reacts with fluorine to form only BrF, $BrF_3$, and $BrF_5$ but not $BrF_7$. The interhalogen compounds are among the most powerful Lewis acids known, with a strong tendency to react with halide ions to give complexes with higher coordination numbers, such as the $IF_8^-$ ion:

$$IF_{7(l)} + KF_{(s)} \rightarrow KIF_{8(s)} \tag{21.5.8}$$

All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7). The interhalogen compounds are also potent oxidants and strong fluorinating agents; contact with organic materials or water can result in an explosion.

> *All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7), but the importance of the higher oxidation states generally decreases down the group.*

**Example 21.5.1**

For each reaction, explain why the given products form.

a. $ClF_3(g) + Cl_2(g) \rightarrow 3ClF(g)$
b. $2KI(s) + 3H_2SO_4(aq) \rightarrow I_2(aq) + SO_2(g) + 2KHSO_4(aq) + 2H_2O(l)$
c. $Pb(s) + 2BrF_3(l) \rightarrow PbF_4(s) + 2BrF(g)$

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

**Solution**

a. When the reactants have the same element in two different oxidation states, we expect the product to have that element in an intermediate oxidation state. We have $Cl^{3+}$ and $Cl^0$ as reactants, so a possible product would have Cl in either the +1 or +2 oxidation state. From our discussion, we know that +1 is much more likely. In this case, $Cl_2$ is behaving like a reductant rather than an oxidant.

b. At first glance, this appears to be a simple acid–base reaction, in which sulfuric acid transfers a proton to $I^-$ to form HI. Recall, however, that $I^-$ can be oxidized to $I_2$. Sulfuric acid contains sulfur in its highest oxidation state (+6), so it is a good oxidant. In this case, the redox reaction predominates.

c. This is the reaction of a metallic element with a very strong oxidant. Consequently, a redox reaction will occur. The only question is whether lead will be oxidized to Pb(II) or Pb(IV). Because $BrF_3$ is a powerful oxidant and fluorine is able to stabilize high oxidation states of other elements, it is likely that $PbF_4$ will be the product. The two possible reduction products for $BrF_3$ are BrF and $Br_2$. The actual product will likely depend on the ratio of the reactants used. With excess $BrF_3$, we expect the more oxidized product (BrF). With lower ratios of oxidant to lead, we would probably obtain $Br_2$ as the product.

**? Exercise 21.5.1**

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow$

b. $GeO_2(s) + HF(aq) \rightarrow$

c. $Fe_2O_3(s) + HCl(g) \xrightarrow{\Delta}$

d. $NaClO_2(aq) + Cl_2(g) \rightarrow$

**Answer**

a. $CaCl_2(s) + H_3PO_4(l) \rightarrow 2HCl(g) + Ca(HPO_4)(soln)$

b. $GeO_2(s) + 6HF(aq) \rightarrow GeF_6^{2-}(aq) + 2H_2O(l) + 2H^+(aq)$

c. $Fe_2O_3(s) + 6HCl(g) \xrightarrow{\Delta} 2FeCl_3(s) + 3H_2O(g)$

d. $2NaClO_2(aq) + Cl_2(g) \rightarrow 2ClO_2(g) + 2NaCl(aq)$

## Summary

The halogens are highly reactive. All halogens have relatively high ionization energies, and the acid strength and oxidizing power of their oxoacids decreases down the group. The halogens are so reactive that none is found in nature as the free element; instead, all but iodine are found as halide salts with the $X^-$ ion. Their chemistry is exclusively that of nonmetals. Consistent with periodic trends, ionization energies decrease down the group. Fluorine, the most reactive element in the periodic table, has a low F–F bond dissociation energy due to repulsions between lone pairs of electrons on adjacent atoms. Fluorine forms ionic compounds with electropositive elements and covalent compounds with less electropositive elements and metals in high oxidation states. All the halogens react with hydrogen to produce hydrogen halides. Except for $F_2$, all react with water to form oxoacids, including the perhalic acids, which contain the halogens in their highest oxidation state. Halogens also form interhalogen compounds; the heavier halogen, with the lower electronegativity, is the central atom.

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# 21.6: The Elements of Group 18 (The Noble Gases)

**Learning Objectives**

- To understand the trends in properties and reactivity of the group 18 elements: the noble gases.

The noble gases were all isolated for the first time within a period of only five years at the end of the 19th century. Their very existence was not suspected until the 18th century, when early work on the composition of air suggested that it contained small amounts of gases in addition to oxygen, nitrogen, carbon dioxide, and water vapor. Helium was the first of the noble gases to be identified, when the existence of this previously unknown element on the sun was demonstrated by new spectral lines seen during a solar eclipse in 1868. Actual samples of helium were not obtained until almost 30 years later, however. In the 1890s, the English physicist J. W. Strutt (Lord Rayleigh) carefully measured the density of the gas that remained after he had removed all $O_2$, $CO_2$, and water vapor from air and showed that this residual gas was slightly denser than pure $N_2$ obtained by the thermal decomposition of ammonium nitrite. In 1894, he and the Scottish chemist William Ramsay announced the isolation of a new "substance" (not necessarily a new element) from the residual nitrogen gas. Because they could not force this substance to decompose or react with anything, they named it argon (Ar), from the Greek argos, meaning "lazy." Because the measured molar mass of argon was 39.9 g/mol, Ramsay speculated that it was a member of a new group of elements located on the right side of the periodic table between the halogens and the alkali metals. He also suggested that these elements should have a preferred valence of 0, intermediate between the +1 of the alkali metals and the −1 of the halogens.

**J. W. Strutt (Lord Rayleigh) (1842–1919)**

Lord Rayleigh was one of the few members of British higher nobility to be recognized as an outstanding scientist. Throughout his youth, his education was repeatedly interrupted by his frail health, and he was not expected to reach maturity. In 1861 he entered Trinity College, Cambridge, where he excelled at mathematics. A severe attack of rheumatic fever took him abroad, but in 1873 he succeeded to the barony and was compelled to devote his time to the management of his estates. After leaving the entire management to his younger brother, Lord Rayleigh was able to devote his time to science. He was a recipient of honorary science and law degrees from Cambridge University.

**Sir William Ramsay (1852–1916)**

Born and educated in Glasgow, Scotland, Ramsay was expected to study for the Calvanist ministry. Instead, he became interested in chemistry while reading about the manufacture of gunpowder. Ramsay earned his PhD in organic chemistry at the University of Tübingen in Germany in 1872. When he returned to England, his interests turned first to physical chemistry and then to inorganic chemistry. He is best known for his work on the oxides of nitrogen and for the discovery of the noble gases with Lord Rayleigh.

In 1895, Ramsey was able to obtain a terrestrial sample of helium for the first time. Then, in a single year (1898), he discovered the next three noble gases: krypton (Kr), from the Greek kryptos, meaning "hidden," was identified by its orange and green emission lines; neon (Ne), from the Greek neos, meaning "new," had bright red emission lines; and xenon (Xe), from the Greek xenos, meaning "strange," had deep blue emission lines. The last noble gas was discovered in 1900 by the German chemist Friedrich Dorn, who was investigating radioactivity in the air around the newly discovered radioactive elements radium and polonium. The element was named radon (Rn), and Ramsay succeeded in obtaining enough radon in 1908 to measure its density (and thus its atomic mass). For their discovery of the noble gases, Rayleigh was awarded the Nobel Prize in Physics and Ramsay the Nobel Prize in Chemistry in 1904. Because helium has the lowest boiling point of any substance known (4.2 K), it is used primarily as a cryogenic liquid. Helium and argon are both much less soluble in water (and therefore in blood) than $N_2$, so scuba divers often use gas mixtures that contain these gases, rather than $N_2$, to minimize the likelihood of the "bends," the painful and potentially fatal formation of bubbles of $N_2(g)$ that can occur when a diver returns to the surface too rapidly.

## Preparation and General Properties of the Group 18 Elements

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth's atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), however, and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either $ns^2np^6$ or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionization energies that decrease smoothly down the group. From their electron affinities, the data in Table 21.6.1 indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidize noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8). These predictions actually summarize the chemistry observed for these elements.

Table 21.6.1: Selected Properties of the Group 18 Elements

| Property | Helium | Neon | Argon | Krypton | Xenon | Radon |
|---|---|---|---|---|---|---|
| atomic symbol | He | Ne | Ar | Kr | Xe | Rn |
| atomic number | 2 | 10 | 18 | 36 | 54 | 86 |
| atomic mass (amu) | 4.00 | 20.18 | 39.95 | 83.80 | 131.29 | 222 |
| valence electron configuration* | $1s^2$ | $2s^22p^6$ | $3s^23p^6$ | $4s^24p^6$ | $5s^25p^6$ | $6s^26p^6$ |
| triple point/boiling point (°C) | —/−269† | −249 (at 43 kPa)/−246 | −189 (at 69 kPa)/−189 | −157/−153 | −112 (at 81.6 kPa)/−108 | −71/−62 |
| density (g/L) at 25°C | 0.16 | 0.83 | 1.63 | 3.43 | 5.37 | 9.07 |
| atomic radius (pm) | 31 | 38 | 71 | 88 | 108 | 120 |
| first ionization energy (kJ/mol) | 2372 | 2081 | 1521 | 1351 | 1170 | 1037 |
| normal oxidation state(s) | 0 | 0 | 0 | 0 (+2) | 0 (+2, +4, +6, +8) | 0 (+2) |
| electron affinity (kJ/mol) | > 0 | > 0 | > 0 | > 0 | > 0 | > 0 |
| electronegativity | — | — | — | — | 2.6 | — |
| product of reaction with $O_2$ | none | none | none | none | not directly with oxygen, but $XeO_3$ can be formed by Equation 21.6.5. | none |
| type of oxide | — | — | — | — | acidic | — |
| product of reaction with $N_2$ | none | none | none | none | none | none |
| product of reaction with $X_2$ | none | none | none | $KrF_2$ | $XeF_2$, $XeF_4$, $XeF_6$ | $RnF_2$ |
| product of reaction with $H_2$ | none | none | none | none | none | none |

*The configuration shown does not include filled d and f subshells. †This is the normal boiling point of He. Solid He does not exist at 1 atm pressure, so no melting point can be given.

## Reactions and Compounds of the Noble Gases

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Figure 21.6.1).

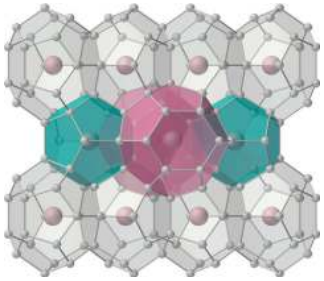


Figure 21.6.1: The Structure of Xenon Hydrate, a Clathrate. Small gaseous atoms or molecules such as Xe or $CH_4$ can occupy cavities in a lattice of hydrogen-bonded water molecules to produce a stable structure with a fixed stoichiometry (in this case, $Xe{\cdot}5.75H_2O$). (The hydrogen atoms of the water molecules have been omitted for clarity.) Warming the solid hydrate or decreasing the pressure of the gas causes it to collapse, with the evolution of gas and the formation of liquid water.

Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules ($H_2O$, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved.

### Methane Clathrates

In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.



Figure 21.6.2: "Burning snowballs." Like xenon, methane ($CH_4$) forms a crystalline clathrate with water: methane hydrate. When the solid is warmed, methane is released and can be ignited to give what appears to be burning snow. (left) Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA (CC-SA-BY-3.0 Wusel007) (middle) A ball-and-stick model of methane hydrate showing the central methane molecule surrounded by a "cage" of water molecules. Other hydrocarbon molecules such as pentane and ethane can occupy the central position in this structure. (United States Department of Energy image). (Right): A burning specimen of methane hydrate ice (United States Geological Survey image).

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that $PtF_6$, a compound used in the Manhattan Project, could oxidize $O_2$. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of $O_2$, Bartlett recognized that $PtF_6$ should also be able to oxidize xenon. When he mixed colorless xenon gas with deep red $PtF_6$ vapor, yellow-orange crystals immediately formed (Figure 21.6.3). Although Bartlett initially postulated that they were $Xe^+PtF_6^-$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the $XeF^+$ ion:

$$Xe\,(g) + PtF_6\,(g) \longrightarrow [XeF^+][PtF_5{}^-]\,(s) \tag{21.6.1}$$

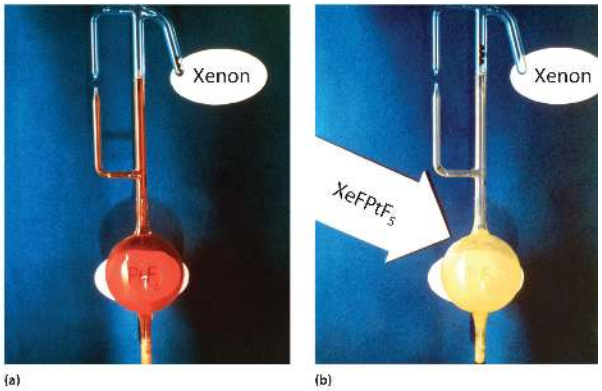



Figure 21.6.3: The Synthesis of the First Chemical Compound of Xenon. (a) An apparatus containing platinum hexafluoride, the red vapor at the bottom left, and xenon, the colorless gas in the small tube at the upper right. (b) When the glass seal separating the two gases is broken and the gases are allowed to mix, a bright yellow solid is formed, which is best described as $XeF^+PtF_5^-$.

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give $XeF_2$, $XeF_4$, or $XeF_6$, depending on conditions; one such reaction is as follows:

$$\mathrm{Xe\,(g) + 2\,F_2\,(g) \longrightarrow XeF_4\,(s)} \tag{21.6.2}$$

The ionization energies of helium, neon, and argon are so high (Table 21.6.1) that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: $F_2$ and $Cl_2$. Although $XeCl_2$ and $KrF_2$ can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

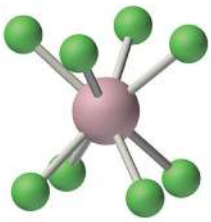
> *The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known.*

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidized immediately on contact, to form anionic complexes. For example, reacting cesium fluoride with $XeF_6$ produces $CsXeF_7$, which gives $Cs_2XeF_8$ when heated:

$$\mathrm{XeF_6\,(s) + CsF\,(s) \longrightarrow CsXeF_7\,(s)} \tag{21.6.3}$$

$$\mathrm{2\,CsXeF_7\,(s) \xrightarrow{\Delta} Cs_2XeF_8\,(s) + XeF_6\,(g)} \tag{21.6.4}$$

The $XeF_8^{2-}$ ion contains eight-coordinate xenon and has the square antiprismatic structure, which is essentially identical to that of the $IF_8^-$ ion. $Cs_2XeF_8$ is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of $Cs_2XeF_8$ are almost certainly the formation of a stable ionic lattice and the **high coordination number** of xenon, which protects the central atom from attack by other species. (Recall from that this latter effect is responsible for the extreme stability of $SF_6$.)




For a previously “inert” gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between $O$ and $Xe$. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either $XeF_4$ or $XeF_6$ produces $XeO_3$, an explosive white solid:

$$\mathrm{XeF_6\,(aq) + 3\,H_2O\,(l) \longrightarrow XeO_3\,(aq) + 6\,HF\,(aq)} \tag{21.6.5}$$

Treating a solution of $XeO_3$ with ozone, a strong oxidant, results in further oxidation of xenon to give either $XeO_4$, a colorless, explosive gas, or the surprisingly stable perxenate ion ($XeO_6^{4-}$), both of which contain xenon in its highest possible oxidation state (+8). The chemistry of the xenon halides and oxides is best understood by analogy to the corresponding compounds of iodine. For example, $XeO_3$ is isoelectronic with the iodate ion ($IO_3^-$), and $XeF_8^{2-}$ is isoelectronic with the $IF_8^-$ ion.

> *Xenon has a high affinity for both fluorine and oxygen.*

Because the ionization energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

### ✔ Example 21.6.1

On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented her major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did she summarize the chemistry of radon?

**Given:** nonradioactive isotope of radon

**Asked for:** summary of its chemistry

**Strategy:**

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics, and kinetics, predict the most likely reactions and compounds of radon.

**Solution**

We expect radon to be significantly easier to oxidize than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidize to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including $RnF_2$, $RnF_4$, $RnF_6$, and possibly $RnF_8$ (due to its large radius). The ion $RnF_8^{2-}$ should also exist. We expect radon to form a series of oxides similar to those of xenon, including $RnO_3$ and possibly $RnO_4$. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

### ? Exercise 21.6.1

Predict the stoichiometry of the product formed by reacting $XeF_6$ with a 1:1 stoichiometric amount of KF and propose a reasonable structure for the anion.

**Answer**

$KXeF_7$; the xenon atom in $XeF_7^-$ has 16 valence electrons, which according to the valence-shell electron-pair repulsion model could give either a square antiprismatic structure with one fluorine atom missing or a pentagonal bipyramid if the $5s^2$ electrons behave like an inert pair that does not participate in bonding.

## Summary

The noble gases are characterized by their high ionization energies and low electron affinities. Potent oxidants are needed to oxidize the noble gases to form compounds in positive oxidation states. The noble gases have a closed-shell valence electron configuration. The ionization energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidized themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

## Contributors and Attributions

- Anonymous

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# 21.E: The p-Block Elements (Exercises)

## Application Problems

1. Borax ($Na_2B_4O_5(OH)_4{\cdot}8H_2O$) is used as a flux during welding operations. As brass is heated during welding, for example, borax cleans the surface of $Cu_2O$ and prevents further oxidation of the fused metal. Explain why borax is effective at cleaning the surface and preventing surface oxidation.
2. Extensive research is being conducted into using GaAs as a material for computer memory chips. It has been found, for example, that chips made from GaAs are up to 10 times faster than those made from silicon. Propose an explanation for this increase in speed.
3. Cement that has a high content of alumina ($Al_2O_3$) is particularly resistant to corrosion, so it is used for structures that must be resistant to seawater and acidic conditions. Why is this material so effective under these service conditions? Failure occurs under prolonged exposure to a hot, wet environment. Why?
4. Aluminum is light and ductile. If you were considering using aluminum rather than steel as a structural material for building a high-speed ferry, what disadvantages would you need to consider in using aluminum for these service conditions?
5. Life on Earth is based on carbon. A possible explanation is that no other element in the periodic table forms compounds that are so diverse in their chemistry and physical properties. Discuss the chemistry of carbon with regard to

    a. types of bonding.
    b. the states of matter of carbon compounds.
    c. the properties of elemental C.
    d. the reactivity of elemental C and its compounds.

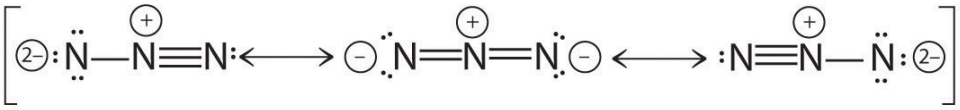
    Then compare B, Al, Si, N, and P with C in terms of these properties.
6. After a traffic accident in which a tanker truck carrying liquid nitrogen overturned, a reporter at the scene warned of a danger to residents in the vicinity of the accident because nitrogen would react with hydrocarbons in the asphalt to produce ammonia gas. Comment on the credibility of this statement.
7. Nitrogen forms a hydride called hydrazoic acid ($HN_3$), which is a colorless, highly toxic, explosive substance that boils at 37°C. The thermal decomposition of one of its salts—$NaN_3$—is used to inflate automotive air bags. The $N_3^-$ ion is isoelectronic with $CO_2$.

    a. Draw the Lewis electron structure of the $N_3^-$ anion.
    b. Write a balanced chemical equation for the thermal decomposition of $NaN_3$.
    c. Based on your answer to part (b), propose an explanation for why many people have suffered skin burns when their air bags exploded.
8. Hydrazine ($N_2H_4$), a rocket fuel, is a colorless, oily liquid with a melting point of 1.4°C, and it is a powerful reducing agent. The physical properties of hydrazine presumably reflect the presence of multiple hydrogen-bond acceptors and donors within a single molecule. Explain the basis for this statement.
9. Because the N–C bond is almost as strong as the N–H bond, organic analogues of ammonia, hydrazine, and hydroxylamine are stable and numerous. Conceptually at least, they are formed by the successive replacement of H atoms by alkyl or aryl groups. Methylhydrazine and dimethylhydrazine, for example, were used as fuels in the US Apollo space program. They react spontaneously and vigorously with liquid $N_2O_4$, thus eliminating the need for an ignition source. Write balanced chemical equations for these reactions and calculate $\Delta G°$ for each reaction.
10. In an effort to remove a troublesome stain from a sink, a member of the cleaning staff of a commercial building first used bleach on the stain and then decided to neutralize the bleach with ammonia. What happened? Why?
11. A slow reaction that occurs on the ocean floor is the conversion of carbonate to bicarbonate, which absorbs $CO_2$. Write a balanced chemical equation for this reaction. Silicate sediments play an important role in controlling the pH of seawater. Given the reaction, propose a chemical explanation for this.
12. Marketing surveys have shown that customers prefer to buy a bright red steak rather than a dull gray one. It is known that NO combines with myoglobin to form a bright red NO complex. What would you add to beef during processing to ensure that this reaction occurs and yields the desired appearance?

13. Covalent azides are used as detonators and explosives. Ionic azides, in contrast, are usually much more stable and are used in dyestuffs. Why is there such a difference between these two types of compounds? The $N_3^-$ ion is considered a pseudohalide. Why?
14. The heads of modern “strike anywhere” matches contain a mixture of a nonvolatile phosphorus sulfide ($P_4S_3$) and an oxidizing agent ($KClO_3$), which is ignited by friction when the match is struck against a rough object. Safety matches separate the oxidant and the reductant by putting $KClO_3$ in the head and a paste containing nonvolatile red phosphorus on the match box or cover. Write a balanced chemical equation for the reaction that occurs when a match is rubbed against the abrasive end of a matchbox.
15. Paris green was a common pigment in paints and wallpaper of the Napoleonic era. It is a mixed acetate/arsenite salt of copper with the formula $Cu_2(OAc)_2(AsO_3)$. In damp conditions, certain fungi are able to convert arsenite salts to volatile, toxic organoarsenic compounds. Shortly after his exile in 1815 to the remote island of St. Helena in the southern Atlantic Ocean, Napoleon died. As a forensic scientist investigating the cause of Napoleon’s mysterious death, you notice that the walls of his enclosed bedchamber are covered in green wallpaper. What chemical clues would you look for to determine the cause of his death?
16. Selenium, an element essential to humans, appears to function biologically in an enzyme that destroys peroxides. Why is selenium especially suited for this purpose? Would sulfur or tellurium be as effective? Why or why not?
17. One way to distinguish between fool’s gold ($FeS_2$, or iron pyrite) and real gold is to heat the sample over a fire. If your sample of “gold” were actually fool’s gold, what would happen?
18. Calcium hypochlorite is sold as swimming pool bleach. It is formed by the hydrolysis of $Cl_2O$, which gives only one product, followed by neutralization with lime [$Ca(OH)_2$]. Write balanced chemical equations for these reactions.
19. There is much interest in the superheavy elements beyond Z = 111 because of their potentially unique properties. Predict the valence electron configurations, preferred oxidation states, and products of the reaction with aqueous acid for elements 113 and 115.
20. Zeolites have become increasingly important in chemical engineering. They can be used as desiccants because the dehydrated zeolite absorbs small molecules, such as water. To be retained by the zeolite frame, a molecule must satisfy two conditions. What are they? Why can linear $CO_2$ and tetrahedral $CH_4$ not be held by a typical zeolite, even though they can penetrate it easily?

## Answers

7. a. Three resonance structures for the azide ion may be reasonably drawn:



b. $2NaN_3(s) \xrightarrow{\Delta} 2Na(s) + 3N_2(g)$

c. One of the products of the decomposition of sodium azide is elemental sodium, which is highly reactive and can ignite in the presence of water and air.

15. Examine samples of Napoleon’s hair and/or fingernails from museums or collections to determine arsenic concentrations.

17. Upon heating, pyrite will react with oxygen to form $SO_2(g)$, which has a pungent smell.

19. Element 113: $5f^{14}6d^{10}7s^27p^1$, +1, $E^+(aq)$; element 115: $5f^{14}6d^{10}7s^27p^3$, +3, $E^{3+}(aq)$

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# CHAPTER OVERVIEW

## 22: The d-Block Elements


22.1: General Trends among the Transition Metals

22.2: A Brief Survey of Transition-Metal Chemistry

22.3: Metallurgy

22.4: Coordination Compounds

22.5: Crystal Field Theory

22.6: Transition Metals in Biology


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# 22.1: General Trends among the Transition Metals

**Learning Objectives**

- To understand the trends in properties and reactivity of the *d*-block elements.

The transition metals, groups 3–12 in the periodic table, are generally characterized by partially filled *d* subshells in the free elements or their cations. (Although the metals of group 12 do not have partially filled *d* shells, their chemistry is similar in many ways to that of the preceding groups, and we therefore include them in our discussion.) Unlike the *s*-block and *p*-block elements, the transition metals exhibit significant horizontal similarities in chemistry in addition to their vertical similarities.

## Electronic Structure and Reactivity of the Transition Metals

The valence electron configurations of the first-row transition metals are given in Table 22.1.1. As we go across the row from left to right, electrons are added to the 3*d* subshell to neutralize the increase in the positive charge of the nucleus as the atomic number increases. With two important exceptions, the 3*d* subshell is filled as expected based on the aufbau principle and Hund's rule. Unexpectedly, however, chromium has a $4s^1 3d^5$ electron configuration rather than the $4s^2 3d^4$ configuration predicted by the aufbau principle, and copper is $4s^1 3d^{10}$ rather than $4s^2 3d^9$. In Chapter 7, we attributed these anomalies to the extra stability associated with half-filled subshells. Because the *ns* and $(n - 1)d$ subshells in these elements are similar in energy, even relatively small effects are enough to produce apparently anomalous electron configurations.

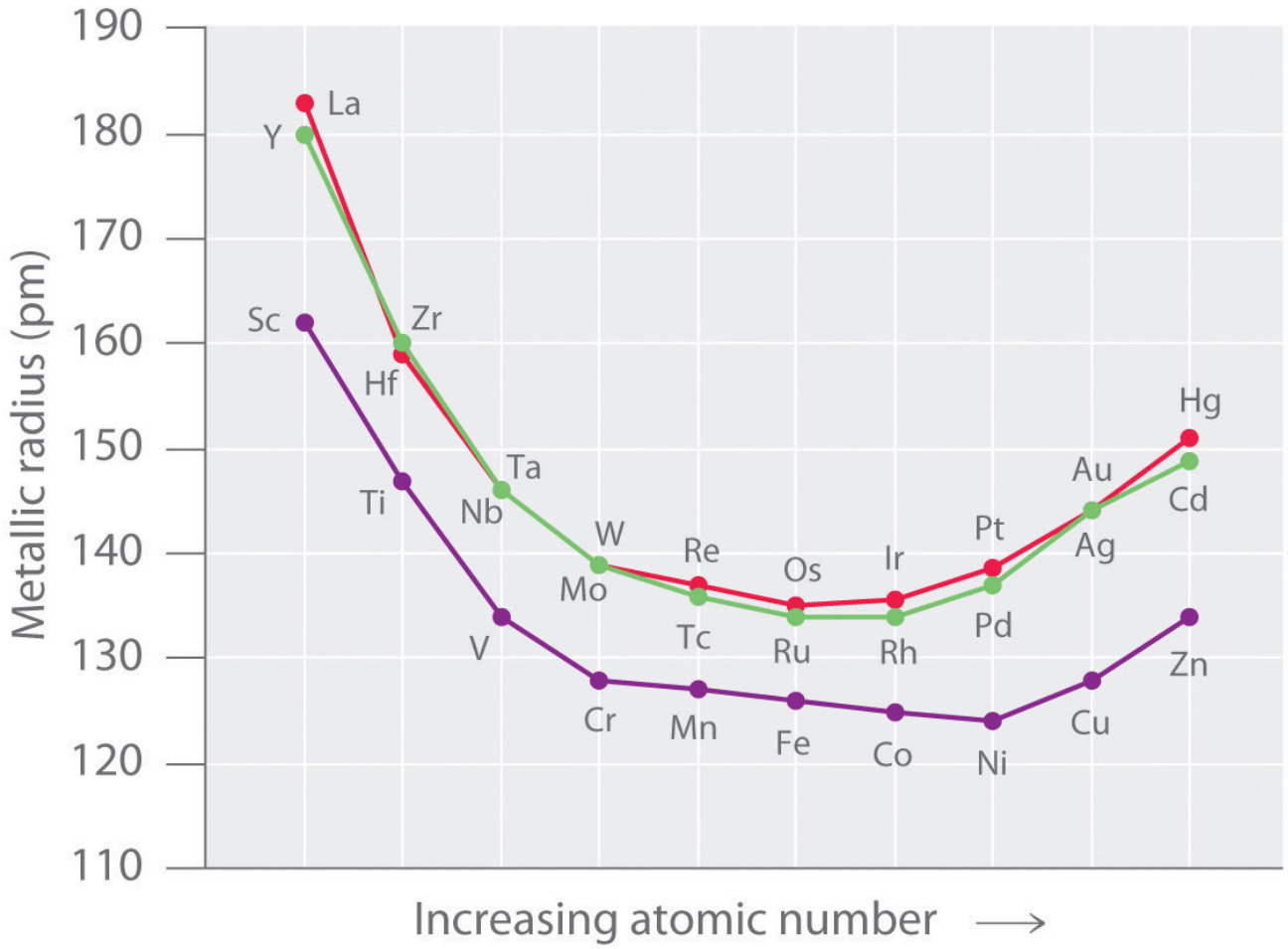
Table 22.1.1 Valence Electron Configurations of the First-Row Transition Metals

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| $4s^2 3d^1$ | $4s^2 3d^2$ | $4s^2 3d^3$ | $4s^1 3d^5$ | $4s^2 3d^5$ | $4s^2 3d^6$ | $4s^2 3d^7$ | $4s^2 3d^8$ | $4s^1 3d^{10}$ | $4s^2 3d^{10}$ |

In the second-row transition metals, electron–electron repulsions within the 4*d* subshell cause additional irregularities in electron configurations that are not easily predicted. For example, Nb and Tc, with atomic numbers 41 and 43, both have a half-filled 5*s* subshell, with $5s^1 4d^4$ and $5s^1 4d^6$ valence electron configurations, respectively. Further complications occur among the third-row transition metals, in which the 4*f*, 5*d*, and 6*s* orbitals are extremely close in energy. Although La has a $6s^2 5d^1$ valence electron configuration, the valence electron configuration of the next element—Ce—is $6s^2 5d^0 4f^2$. From this point through element 71, added electrons enter the 4*f* subshell, giving rise to the 14 elements known as the lanthanides. After the 4*f* subshell is filled, the 5*d* subshell is populated, producing the third row of the transition metals. Next comes the seventh period, where the actinides have three subshells (7*s*, 6*d*, and 5*f*) that are so similar in energy that their electron configurations are even more unpredictable.

As we saw in the *s*-block and *p*-block elements, the size of neutral atoms of the *d*-block elements gradually decreases from left to right across a row, due to an increase in the effective nuclear charge ($Z_{eff}$) with increasing atomic number. In addition, the atomic radius increases down a group, just as it does in the *s* and *p* blocks. Because of the *lanthanide contraction*, however, the increase in size between the 3*d* and 4*d* metals is much greater than between the 4*d* and 5*d* metals (Figure 22.1.1. (For more information on the lanthanides, see Chapter 7, Section 7.3.) The effects of the lanthanide contraction are also observed in ionic radii, which explains why, for example, there is only a slight increase in radius from $Mo^{3+}$ to $W^{3+}$.

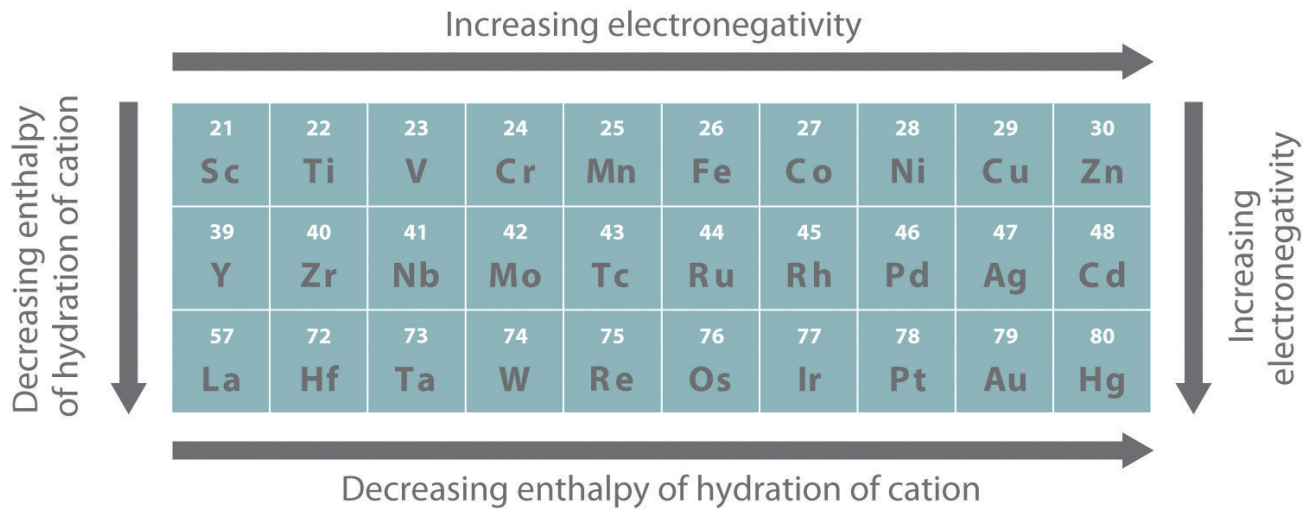
Figure 22.1.1 *The Metallic Radii of the First-, Second-, and Third-Row Transition Metals*




*Because of the lanthanide contraction, the second- and third-row transition metals are very similar in size.*

As you learned in Chapter 7, electrons in $(n - 1)d$ and $(n - 2)f$ subshells are only moderately effective at shielding the nuclear charge; as a result, the effective nuclear charge experienced by valence electrons in the *d*-block and *f*-block elements does not change greatly as the nuclear charge increases across a row. Consequently, the ionization energies of these elements increase very slowly across a given row (Figure 7.10). In addition, as we go from the top left to the bottom right corner of the *d* block, electronegativities generally increase, densities and electrical and thermal conductivities increase, and enthalpies of hydration of the metal cations decrease in magnitude, as summarized in Figure 22.1.2. Consistent with this trend, the transition metals become steadily less reactive and more "noble" in character from left to right across a row. The relatively high ionization energies and electronegativities and relatively low enthalpies of hydration are all major factors in the noble character of metals such as Pt and Au.

Figure 22.1.2 *Some Trends in Properties of the Transition Metals*




*The electronegativity of the elements increases, and the hydration energies of the metal cations decrease in magnitude from left to right and from top to bottom of the d block. As a result, the metals in the lower right corner of the d block are so unreactive that they are often called the "noble metals."*

## Trends in Transition Metal Oxidation States

The similarity in ionization energies and the relatively small increase in successive ionization energies lead to the formation of metal ions with the same charge for many of the transition metals. This in turn results in extensive horizontal similarities in chemistry, which are most noticeable for the first-row transition metals and for the lanthanides and actinides. Thus all the first-row transition metals except Sc form stable compounds that contain the 2+ ion, and, due to the small difference between the second and third ionization energies for these elements, all except Zn also form stable compounds that contain the 3+ ion. The relatively small increase in successive ionization energies causes most of the transition metals to exhibit multiple oxidation states separated by a single electron. Manganese, for example, forms compounds in every oxidation state between −3 and +7. Because of the slow but steady increase in ionization potentials across a row, high oxidation states become progressively less stable for the elements on the right side of the *d* block. The occurrence of multiple oxidation states separated by a single electron causes many, if not most, compounds of the transition metals to be paramagnetic, with one to five unpaired electrons. This behavior is in sharp contrast to that of the *p*-block elements, where the occurrence of two oxidation states separated by two electrons is common, which makes virtually all compounds of the *p*-block elements diamagnetic.

### Note the Pattern

Due to a small increase in successive ionization energies, most of the transition metals have multiple oxidation states separated by a single electron.

### Note the Pattern:

Most compounds of transition metals are paramagnetic, whereas virtually all compounds of the *p*-block elements are diamagnetic.

The electronegativities of the first-row transition metals increase smoothly from Sc ($\chi$ = 1.4) to Cu ($\chi$ = 1.9). Thus Sc is a rather active metal, whereas Cu is much less reactive. The steady increase in electronegativity is also reflected in the standard reduction potentials: thus $E°$ for the reaction $M^{2+}(aq) + 2e^- \rightarrow M^0(s)$ becomes progressively less negative from Ti ($E° = -1.63$ V) to Cu ($E° = +0.34$ V). Exceptions to the overall trends are rather common, however, and in many cases, they are attributable to the stability associated with filled and half-filled subshells. For example, the $4s^23d^{10}$ electron configuration of zinc results in its strong tendency to form the stable $Zn^{2+}$ ion, with a $3d^{10}$ electron configuration, whereas $Cu^+$, which also has a $3d^{10}$ electron configuration, is the only stable monocation formed by a first-row transition metal. Similarly, with a half-filled subshell, $Mn^{2+}$ ($3d^5$) is much more difficult to oxidize than $Fe^{2+}$ ($3d^6$). The chemistry of manganese is therefore primarily that of the $Mn^{2+}$ ion, whereas both the $Fe^{2+}$ and $Fe^{3+}$ ions are important in the chemistry of iron.

The transition metals form cations by the initial loss of the *ns* electrons of the metal, even though the *ns* orbital is *lower* in energy than the $(n - 1)d$ subshell in the neutral atoms. This apparent contradiction is due to the small difference in energy between the *ns* and $(n - 1)d$ orbitals, together with screening effects. The loss of one or more electrons reverses the relative energies of the *ns* and $(n - 1)d$ subshells, making the latter lower in energy. Consequently, *all transition-metal cations possess* $d^n$ *valence electron configurations*, as shown in Table 22.1.2 for the 2+ ions of the first-row transition metals.

### Note the Pattern

All transition-metal cations have $d^n$ electron configurations; the *ns* electrons are *always* lost *before* the $(n - 1)d$ electrons.

Table 22.1.2 *d*-Electron Configurations of the Dications of the First-Row Transition Metals

| $Ti^{2+}$ | $V^{2+}$ | $Cr^{2+}$ | $Mn^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ |
|---|---|---|---|---|---|---|---|---|
| $d^2$ | $d^3$ | $d^4$ | $d^5$ | $d^6$ | $d^7$ | $d^8$ | $d^9$ | $d^{10}$ |

The most common oxidation states of the first-row transition metals are shown in Table 22.1.3. The second- and third-row transition metals behave similarly but with three important differences:

1. The maximum oxidation states observed for the second- and third-row transition metals in groups 3–8 increase from +3 for Y and La to +8 for Ru and Os, corresponding to the formal loss of all *ns* and $(n - 1)d$ valence electrons. As we go farther to the right, the maximum oxidation state decreases steadily, reaching +2 for the elements of group 12 (Zn, Cd, and Hg), which corresponds to a filled $(n - 1)d$ subshell.
2. Within a group, higher oxidation states become more stable down the group. For example, the chromate ion ($[CrO_4]^{2-}$) is a powerful oxidant, whereas the tungstate ion ($[WO_4]^{2-}$) is extremely stable and has essentially no tendency to act as an oxidant.
3. Cations of the second- and third-row transition metals in lower oxidation states (+2 and +3) are much more easily oxidized than the corresponding ions of the first-row transition metals. For example, the most stable compounds of chromium are those of Cr(III), but the corresponding Mo(III) and W(III) compounds are highly reactive. In fact, they are often *pyrophoric*, bursting into flames on contact with atmospheric oxygen. As we shall see, the heavier elements in each group form stable compounds in higher oxidation states that have no analogues with the lightest member of the group.

### Note the Pattern

The highest possible oxidation state, corresponding to the formal loss of all valence electrons, becomes increasingly less stable as we go from group 3 to group 8, and it is never observed in later groups.

### Note the Pattern

In the transition metals, the stability of higher oxidation states increases down a column.

Table 22.1.3 Common Oxidation States of the First-Row Transition Metals*

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| electronic structure | $s^2d^1$ | $s^2d^2$ | $s^2d^3$ | $s^1d^5$ | $s^2d^5$ | $s^2d^6$ | $s^2d^7$ | $s^2d^8$ | $s^1d^{10}$ | $s^2d^{10}$ |
| oxidation states | | | | I | | | | | I | |
| | | II | II | II | II | II | II | II | II | II |
| | III | III | III | III | III | III | III | III | III | |
| | | IV | IV | IV | IV | IV | IV | IV | | |
| | | | V | V | V | V | V | | | |
| | | | | VI | VI | VI | | | | |
| | | | | | VII | | | | | |

*The convention of using roman numerals to indicate the oxidation states of a metal is used here.

Binary transition-metal compounds, such as the oxides and sulfides, are usually written with idealized stoichiometries, such as FeO or FeS, but these compounds are usually cation deficient and almost never contain a 1:1 cation:anion ratio. Thus a substance such as ferrous oxide is actually a nonstoichiometric compound with a range of compositions.

The acid–base character of transition-metal oxides depends strongly on the oxidation state of the metal and its ionic radius. Oxides of metals in lower oxidation states (less than or equal to +3) have significant ionic character and tend to be basic. Conversely, oxides of metals in higher oxidation states are more covalent and tend to be acidic, often dissolving in strong base to form oxoanions.

### EXAMPLE 1

Two of the group 8 metals (Fe, Ru, and Os) form stable oxides in the +8 oxidation state. Identify these metals; predict the stoichiometry of the oxides; describe the general physical and chemical properties, type of bonding, and physical state of the oxides; and decide whether they are acidic or basic oxides.

**Given:** group 8 metals

**Asked for:** identity of metals and expected properties of oxides in +8 oxidation state

**Strategy:**

Refer to the trends outlined in Figure 22.1.1, Figure 22.1.1, Table 22.1.2, Table 22.1.2, and Table 22.1.3 to identify the metals. Decide whether their oxides are covalent or ionic in character, and, based on this, predict the general physical and chemical properties of the oxides.

**Solution:**

The +8 oxidation state corresponds to a stoichiometry of $MO_4$. Because the heavier transition metals tend to be stable in higher oxidation states, we expect Ru and Os to form the most stable tetroxides. Because oxides of metals in high oxidation states are generally covalent compounds, $RuO_4$ and $OsO_4$ should be volatile solids or liquids that consist of discrete $MO_4$ molecules, which the valence-shell electron-pair repulsion (VSEPR) model predicts to be tetrahedral. Finally, because oxides of transition metals in high oxidation states are usually acidic, $RuO_4$ and $OsO_4$ should dissolve in strong aqueous base to form oxoanions.

### ? Exercise 22.1.1

Predict the identity and stoichiometry of the stable group 9 bromide in which the metal has the lowest oxidation state and describe its chemical and physical properties.

**Answer**

Because the lightest element in the group is most likely to form stable compounds in lower oxidation states, the bromide will be $CoBr_2$. We predict that $CoBr_2$ will be an ionic solid with a relatively high melting point and that it will dissolve in water to give the $Co^{2+}(aq)$ ion.

## Summary

The transition metals are characterized by partially filled *d* subshells in the free elements and cations. The *ns* and $(n - 1)d$ subshells have similar energies, so small influences can produce electron configurations that do not conform to the general order in which the subshells are filled. In the second- and third-row transition metals, such irregularities can be difficult to predict, particularly for the third row, which has 4*f*, 5*d*, and 6*s* orbitals that are very close in energy. The increase in atomic radius is greater between the 3*d* and 4*d* metals than between the 4*d* and 5*d* metals because of the lanthanide contraction. Ionization energies and electronegativities increase slowly across a row, as do densities and electrical and thermal conductivities, whereas enthalpies of hydration decrease. Anomalies can be explained by the increased stabilization of half-filled and filled subshells. Transition-metal cations are formed by the initial loss of *ns* electrons, and many metals can form cations in several oxidation states. Higher oxidation states become progressively less stable across a row and more stable down a column. Oxides of small, highly charged metal ions tend to be acidic, whereas oxides of metals with a low charge-to-radius ratio are basic.

## KEY TAKEAWAYS

- Transition metals are characterized by the existence of multiple oxidation states separated by a single electron.
- Most transition-metal compounds are paramagnetic, whereas virtually all compounds of the *p*-block elements are diamagnetic.

## CONCEPTUAL PROBLEMS

1. The transition metals show significant horizontal similarities in chemistry in addition to their vertical similarities, whereas the same cannot be said of the *s*-block and *p*-block elements. Explain why this is so.
2. The energy of the *d* subshell does not change appreciably in a given period. Why? What effect does this have on the ionization potentials of the transition metals? on their electronegativities?
3. Standard reduction potentials vary across the first-row transition metals. What effect does this have on the chemical reactivity of the first-row transition metals? Which two elements in this period are more active than would be expected? Why?
4. Many transition metals are paramagnetic (have unpaired electrons). How does this affect electrical and thermal conductivities across the rows?
5. What is the lanthanide contraction? What effect does it have on the radii of the transition metals of a given group? What effect does it have on the chemistry of the elements in a group?
6. Why are the atomic volumes of the transition elements low compared with the elements of groups 1 and 2? Ir has the highest density of any element in the periodic table (22.65 $g/cm^3$). Why?
7. Of the elements Ti, Ni, Cu, and Cd, which do you predict has the highest electrical conductivity? Why?
8. The chemistry of As is most similar to the chemistry of which transition metal? Where in the periodic table do you find elements with chemistry similar to that of Ge? Explain your answers.
9. The coinage metals (group 11) have significant noble character. In fact, they are less reactive than the elements of group 12. Explain why this is so, referring specifically to their reactivity with mineral acids, electronegativity, and ionization energies. Why are the group 12 elements more reactive?

## STRUCTURE AND REACTIVITY

1. Give the valence electron configurations of the 2+ ion for each first-row transition element. Which two ions do you expect to have the most negative $E°$ value? Why?
2. Arrange $Ru^{3+}$, $Cu^{2+}$, Zn, $Ti^{4+}$, $Cr^{3+}$, and $Ni^{2+}$ in order of increasing radius.
3. Arrange $Pt^{4+}$, $Hg^{2+}$, $Fe^{2+}$, $Zr^{4+}$, and $Fe^{3+}$ in order of decreasing radius.
4. Of $Ti^{2+}$, $V^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Zn^{2+}$, which divalent ion has the smallest ionic radius? Explain your reasoning.

## AnswerS

1. $Ti^{2+}$, $3d^2$; $V^{2+}$, $3d^3$; $Cr^{2+}$, $3d^4$; $Mn^{2+}$, $3d^5$; $Fe^{2+}$, $3d^6$; $Co^{2+}$, $3d^7$; $Ni^{2+}$, $3d^8$; $Cu^{2+}$, $3d^9$; $Zn^{2+}$, $3d^{10}$. Because $Z_{eff}$ increases from left to right, $Ti^{2+}$ and $V^{2+}$ will have the most negative reduction potentials (be most difficult to reduce).
2.

3. $Hg^{2+} > Fe^{2+} > Zr^{4+} > Fe^{3+} > Pt^{4}$

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# 22.2: A Brief Survey of Transition-Metal Chemistry

**Learning Objectives**

- To use periodic trends to understand the chemistry of the transition metals.

As we shall see, the two heaviest members of each group usually exhibit substantial similarities in chemical behavior and are quite different from the lightest member.

## Group 3 (Sc, Y, La, and Ac)

As shown in Table 22.2.1, the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n-1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. As expected based on periodic trends, these elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

$$2M_{(s)} + 6H_2O_{(l)} \rightarrow 2M(OH)_{3(s)} + 3H_{2(g)} \tag{22.2.1}$$

> *The chemistry of the group 3 metals is almost exclusively that of the $M^{3+}$ ion; the elements are powerful reductants.*

Moreover, all dissolve readily in aqueous acid to produce hydrogen gas and a solution of the hydrated metal ion: $M^{3+}(aq)$.

Table 22.2.1: Some Properties of the Elements of Groups 3, 4, and 5

| Group | Element | Z | Valence Electron Configuration | Electronegativity | Metallic Radius (pm) | Melting Point (°C) | Density ($g/cm^3$) |
|---|---|---|---|---|---|---|---|
| 3 | Sc | 21 | $4s^23d^1$ | 1.36 | 162 | 1541 | 2.99 |
| | Y | 39 | $5s^24d^1$ | 1.22 | 180 | 1522 | 4.47 |
| | La | 57 | $6s^25d^1$ | 1.10 | 183 | 918 | 6.15 |
| | Ac | 89 | $7s^26d^1$ | 1.10 | 188 | 1051 | 10.07 |
| 4 | Ti | 22 | $4s^23d^2$ | 1.54 | 147 | 1668 | 4.51 |
| | Zr | 40 | $5s^24d^2$ | 1.33 | 160 | 1855 | 6.52 |
| | Hf | 72 | $6s^25d^24f^{14}$ | 1.30 | 159 | 2233 | 13.31 |
| 5 | V | 23 | $4s^23d^3$ | 1.63 | 134 | 1910 | 6.00 |
| | Nb | 41 | $5s^24d^3$ | 1.60 | 146 | 2477 | 8.57 |
| | Ta | 73 | $6s^25d^34f^{14}$ | 1.50 | 146 | 3017 | 16.65 |

The group 3 metals react with nonmetals to form compounds that are primarily ionic in character. For example, reacting group 3 metals with the halogens produces the corresponding trihalides: $MX_3$. The trifluorides are insoluble in water because of their high lattice energies, but the other trihalides are very soluble in water and behave like typical ionic metal halides. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called sesquioxides ($M_2O_3$), which react with $H_2O$ or $CO_2$ to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but "mischmetal," a mixture of lanthanides containing about 40% La, is used as an additive to improve the properties of steel and make flints for cigarette lighters.

## Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

$$2FeTiO_{3(s)} + 6C_{(s)} + 7Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + 2FeCl_{3(g)} + 6CO_{(g)} \tag{22.2.2}$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

> *The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.*

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in $UO_2$-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Figure 23.2, the group 4 metals become denser, higher melting, and more electropositive down the column (Table 22.2.1). Unexpectedly, however, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of $Ti^{2+}$ are usually powerful reductants. In fact, the $Ti^{2+}(aq)$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides ($MX_4$), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides ($MO_2$) and dichalcogenides ($MY_2$). Industrially, $TiO_2$, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

$$TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)} \tag{22.2.3}$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure 22.2.1). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as $TiH_2$), nitrides (such as TiN), carbides (such as TiC), and borides (such as $TiB_2$), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

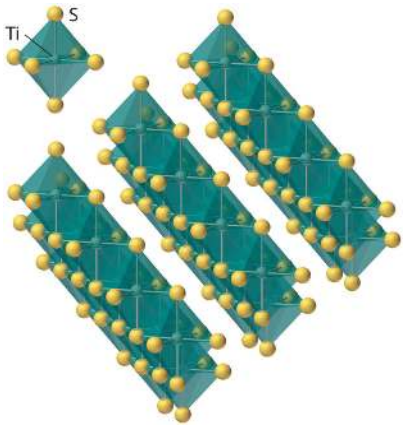



Figure 22.2.1: The Layered Structure of $TiS_2$. Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.

## Group 5 (V, Nb, and Ta)

Like the group 4 elements, all group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is so similar that these elements are usually found in the same ores.

Three-fourths of the vanadium produced annually is used in the production of steel alloys for springs and high-speed cutting tools. Adding a small amount of vanadium to steel results in the formation of small grains of $V_4C_3$, which greatly increase the strength and resilience of the metal, especially at high temperatures. The other major use of vanadium is as $V_2O_5$, an important catalyst for the industrial conversion of $SO_2$ to $SO_3$ in the contact process for the production of sulfuric acid. In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. Although niobium is used as an additive in certain stainless steels, its primary application is in superconducting wires such as $Nb_3Zr$ and $Nb_3Ge$, which are used in superconducting magnets for the magnetic resonance imaging of soft tissues. Because tantalum is highly resistant to corrosion, it is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

> *The chemistry of the two heaviest group 5 metals (Nb and Ta) is dominated by the +5 oxidation state. The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.*

As indicated in Table 22.2.1, the trends in properties of the group 5 metals are similar to those of group 4. Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, vanadium is the only element in the group that forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen, however, to produce the corresponding oxides in the +5 oxidation state ($M_2O_5$), in which polarization of the oxide ions by the high-oxidation-state metal is so extensive that the compounds are primarily covalent in character. Vanadium–oxygen species provide a classic example of the effect of increasing metal oxidation state on the protonation state of a coordinated water molecule: vanadium(II) in water exists as the violet hydrated ion $[V(H_2O)_6]^{2+}$; the blue-green $[V(H_2O)_6]^{3+}$ ion is acidic, dissociating to form small amounts of the $[V(H_2O)_5(OH)]^{2+}$ ion and a proton; and in water, vanadium(IV) forms the blue vanadyl ion $[(H_2O)_4VO]^{2+}$, which contains a formal V=O bond (Figure 22.2.2). Consistent with its covalent character, $V_2O_5$ is acidic, dissolving in base to give the vanadate ion ($[VO_4]^{3-}$), whereas both $Nb_2O_5$ and $Ta_2O_5$ are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Because vanadium ions with different oxidation states have different numbers of d electrons, aqueous solutions of the ions have different colors: in acid V(V) forms the pale yellow $[VO_2]^+$ ion; V(IV) is the blue vanadyl ion $[VO]^{2+}$; and V(III) and V(II) exist as the hydrated $V^{3+}$ (blue-green) and $V^{2+}$ (violet) ions, respectively.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important are the dichalcogenides ($MY_2$), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

## Group 6 (Cr, Mo, and W)

As an illustration of the trend toward increasing polarizability as we go from left to right across the d block, in group 6 we first encounter a metal (Mo) that occurs naturally as a sulfide ore rather than as an oxide. Molybdenite ($MoS_2$) is a soft black mineral that can be used for writing, like PbS and graphite. Because of this similarity, people long assumed that these substances were all the same. In fact, the name molybdenum is derived from the Greek molybdos, meaning “lead.” More than 90% of the molybdenum produced annually is used to make steels for cutting tools, which retain their sharp edge even when red hot. In addition, molybdenum is the only second- or third-row transition element that is essential for humans. The major chromium ore is chromite ($FeCr_2O_4$), which is oxidized to the soluble $[CrO_4]^{2-}$ ion under basic conditions and reduced successively to $Cr_2O_3$ and Cr with carbon and aluminum, respectively. Pure chromium can be obtained by dissolving $Cr_2O_3$ in sulfuric acid followed by electrolytic reduction; a similar process is used for electroplating metal objects to give them a bright, shiny, protective surface layer. Pure tungsten is obtained by first converting tungsten ores to $WO_3$, which is then reduced with hydrogen to give the metal.

> *The metals become increasing polarizable across the d block.*

Consistent with periodic trends, the group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 22.2.2). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to extensive polarization of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from $Cr^{2+}$, which is a powerful reductant, to $CrO_3$, a red solid that is a powerful oxidant. For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

Table 22.2.2: Some Properties of the Elements of Groups 6 and 7

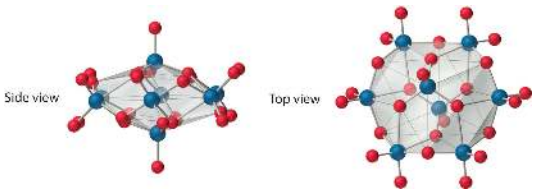
| Group | Element | Z | Valence Electron Configuration | Electronegativity | Metallic Radius (pm) | Melting Point (°C) | Density ($g/cm^3$) |
|---|---|---|---|---|---|---|---|
| 6 | Cr | 24 | $4s^1 3d^5$ | 1.66 | 128 | 1907 | 7.15 |
| | Mo | 42 | $5s^1 4d^5$ | 2.16 | 139 | 2623 | 10.20 |
| | W | 74 | $6s^2 5d^4 4f^{14}$ | 1.70 | 139 | 3422 | 19.30 |
| 7 | Mn | 25 | $4s^2 3d^5$ | 1.55 | 127 | 1246 | 7.30 |
| | Tc | 43 | $5s^2 4d^5$ | 2.10 | 136 | 2157 | 11.50 |
| | Re | 75 | $6s^2 5d^5 4f^{14}$ | 1.90 | 137 | 3186 | 20.80 |

> The chemistry of the two heaviest group 6 metals (Mo and W) is dominated by the +6 oxidation state. The chemistry of the lightest element (Cr) is dominated by lower oxidation states.

As observed in previous groups, the group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases, and their melting points decrease. Recall that as the electronegativity of the halogens decreases from F to I, they are less able to stabilize high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but $CrF_6$ is unstable at temperatures above −100°C, whereas $MoF_6$ and $WF_6$ are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-row elements,

the other halogens can oxidize chromium to only the trihalides, $CrX_3$ (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and $MoI_3$, and tungsten gives $WCl_6$, $WBr_5$, and $WI_4$.

Both Mo and W react with oxygen to form the covalent trioxides ($MoO_3$ and $WO_3$), but Cr reacts to form only the so-called sesquioxide ($Cr_2O_3$). Chromium will form $CrO_3$, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in base to form the corresponding oxoanions ($[MO_4]^{2-}$). Consistent with periodic trends, the sesquioxide of the lightest element in the group ($Cr_2O_3$) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH they form a series of polymeric anions called isopolymetallates, such as the $[Mo_8O_{26}]^{4-}$ ion, whose structure is as follows:




An isopolymolybdate cluster. The $[Mo_8O_{26}]^{4-}$ ion, shown here in both side and top views, is typical of the oxygen-bridged clusters formed by Mo(VI) and W(VI) in aqueous solution.

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is $MoS_2$; it has a layered structure similar to that of $TiS_2$ (Figure 22.2.1), in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both $MoS_2$ and $WS_2$ are used as lubricants in a variety of applications, including automobile engines. Because tungsten itself has an extraordinarily high melting point (3380°C), lubricants described as containing "liquid tungsten" actually contain a suspension of very small $WS_2$ particles.

As in groups 4 and 5, the elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

## Group 7 (Mn, Tc, and Re)

Continuing across the periodic table, we encounter the group 7 elements (Table 22.2.2). One group 7 metal (Mn) is usually combined with iron in an alloy called ferromanganese, which has been used since 1856 to improve the mechanical properties of steel by scavenging sulfur and oxygen impurities to form MnS and MnO. Technetium is named after the Greek technikos, meaning "artificial," because all its isotopes are radioactive. One isotope, $^{99m}Tc$ (m for metastable), has become an important biomedical tool for imaging internal organs. Because of its scarcity, Re is one of the most expensive elements, and its applications are limited. It is, however, used in a bimetallic Pt/Re catalyst for refining high-octane gasoline.

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from −3 to +7 are known, with the most common being +2 and +4 (Figure 22.2.3). In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive. In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configuration, the aqueous $Mn^{3+}$ ion, with a $3d^4$ valence electron configuration, is a potent oxidant that is able to oxidize water. It is difficult to generalize about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Like vanadium, compounds of manganese in different oxidation states have different numbers of d electrons, which leads to compounds with different colors: the $Mn^{2+}(aq)$ ion is pale pink; $Mn(OH)_3$, which contains Mn(III), is a dark brown solid; $MnO_2$, which contains Mn(IV), is a black solid; and aqueous solutions of Mn(VI) and Mn(VII) contain the green manganate ion $[MnO_4]^{2-}$ and the purple permanganate ion $[MnO_4]^-$, respectively.

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with $F_2$ gives only $MnF_3$, a high-melting, red-purple solid, whereas Re reacts with $F_2$ to give $ReF_7$, a volatile, low-melting, yellow solid. Again, reaction with

the less oxidizing, heavier halogens produces halides in lower oxidation states. Thus reaction with $Cl_2$, a weaker oxidant than $F_2$, gives $MnCl_2$ and $ReCl_6$. Reaction of Mn with oxygen forms only $Mn_3O_4$, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite ($Fe_3O_4$). In contrast, Tc and Re form high-valent oxides, the so-called heptoxides ($M_2O_7$), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Under forced conditions, manganese will form $Mn_2O_7$, an unstable, explosive, green liquid. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of $MoS_2$, as well as more complex heptasulfides ($M_2S_7$). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

> *The chemistry of the group 7 metals (Mn, Tc, and Re) is dominated by lower oxidation states. Compounds in the maximum possible oxidation state (+7) are readily reduced.*

## Groups 8, 9, and 10

In many older versions of the periodic table, groups 8, 9, and 10 were combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry, in addition to the similarities within each column. In part, these horizontal similarities are due to the fact that the ionization potentials of the elements, which increase slowly but steadily across the d block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10). As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3 for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called precious metals because they are rather rare in nature and mostly chemically inert.

> *The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.*

### Group 8 (Fe, Ru, and Os)

The chemistry of group 8 is dominated by iron, whose high abundance in Earth's crust is due to the extremely high stability of its nucleus. Ruthenium and osmium, on the other hand, are extremely rare elements, with terrestrial abundances of only about 0.1 ppb and 5 ppb, respectively, and they were not discovered until the 19th century. Because of the high melting point of iron (1538°C), early humans could not use it for tools or weapons. The advanced techniques needed to work iron were first developed by the Hittite civilization in Asia Minor sometime before 2000 BC, and they remained a closely guarded secret that gave the Hittites military supremacy for almost a millennium. With the collapse of the Hittite civilization around 1200 BC, the technology became widely distributed, however, leading to the Iron Age.

### Group 9 (Co, Rh, and Ir)

Cobalt is one of the least abundant of the first-row transition metals. Its oxide ores, however, have been used in glass and pottery for thousands of years to produce the brilliant color known as "cobalt blue," and its compounds are consumed in large quantities in the paint and ceramics industries. The heavier elements of group 9 are also rare, with terrestrial abundances of less than 1 ppb; they are generally found in combination with the heavier elements of groups 8 and 10 in Ni–Cu–S ores.

### Group 10 (Ni, Pd, and Pt)

Nickel silicates are easily processed; consequently, nickel has been known and used since antiquity. In fact, a 75:25 Cu:Ni alloy was used for more than 2000 years to mint "silver" coins, and the modern US nickel uses the same alloy. In contrast to nickel, palladium and platinum are rare (their terrestrial abundance is about 10–15 ppb), but they are at least an order of magnitude more abundant than the heavier elements of groups 8 and 9. Platinum and palladium are used in jewelry, the former as the pure element and the latter as the Pd/Au alloy known as white gold.



*Over 2000 years ago, the Bactrian civilization in Western Asia used a 75:25 alloy of copper and nickel for its coins. A modern US nickel has the same composition, but a modern Canadian nickel is nickel-plated steel and contains only 2.5% nickel by mass.*

## Trends in Group 8, 9, and 10

Some properties of the elements in groups 8–10 are summarized in Table 22.2.3. As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. We are now at the point in the d block where there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation state formed by losing the ns2 valence electrons. In addition, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 22.2.3: Some Properties of the Elements of Groups 8, 9, and 10

| Group | Element | Z | Valence Electron Configuration | Electronegativity | Metallic Radius (pm) | Melting Point (°C) | Density ($g/cm^3$) |
|---|---|---|---|---|---|---|---|
| 8 | Fe | 26 | $4s^2 3d^6$ | 1.83 | 126 | 1538 | 7.87 |
| | Ru | 44 | $5s^1 4d^7$ | 2.20 | 134 | 2334 | 12.10 |
| | Os | 76 | $6s^2 5d^6 4f^{14}$ | 2.20 | 135 | 3033 | 22.59 |
| 9 | Co | 27 | $4s^2 3d^7$ | 1.88 | 125 | 1495 | 8.86 |
| | Rh | 45 | $5s^1 4d^8$ | 2.28 | 134 | 1964 | 12.40 |
| | Ir | 77 | $6s^2 5d^7 4f^{14}$ | 2.20 | 136 | 2446 | 22.50 |
| 10 | Ni | 28 | $4s^2 3d^8$ | 1.91 | 124 | 1455 | 8.90 |
| | Pd | 46 | $4d^{10}$ | 2.20 | 137 | 1555 | 12.00 |
| | Pt | 78 | $6s^2 5d^8 4f^{14}$ | 2.20 | 139 | 1768 | 21.50 |

We stated that higher oxidation states become less stable as we go across the d-block elements and more stable as we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride $NiF_2$. In contrast to Fe, Ru and Os form a series of fluorides up to $RuF_6$ and $OsF_7$. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, $Fe_2O_3$, and the mixed-valent $Fe_3O_4$ (magnetite), all of which are nonstoichiometric. In contrast, Ru and Os form the dioxides ($MO_2$) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases rapidly as we go farther across the d block.

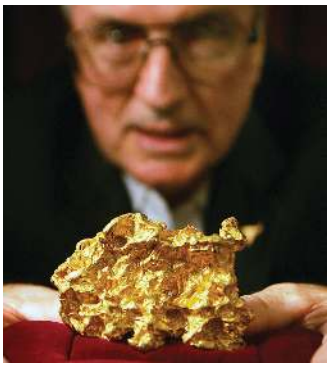
> *Higher oxidation states become less stable across the d-block, but more stable down a group.*

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion ($S_2^{2-}$), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions ($S^{2-}$). This combination of highly charged cations and easily polarized anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far the most important of these is cementite ($Fe_3C$), which is used to strengthen steel. At high temperatures, $Fe_3C$ is soluble in iron, but slow cooling causes the phases to separate and form particles of cementite, which gives a metal that retains much of its strength but is significantly less brittle than pure iron. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to $H_2$ but essentially impermeable to all other gases, including He. Consequently, diffusion of $H_2$ through Pd is an effective method for separating hydrogen from other gases.

## Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally (like the gold nugget shown here); consequently, these were probably the first metals used by ancient humans. For example, decorative gold artifacts dating from the late Stone Age are known, and some gold Egyptian coins are more than 5000 yr old. Copper is almost as ancient, with objects dating to about 5000 BC. Bronze, an alloy of copper and tin that is harder than either of its constituent metals, was used before 3000 BC, giving rise to the Bronze Age. Deposits of silver are much less common than deposits of gold or copper, yet by 3000 BC, methods had been developed for recovering silver from its ores, which allowed silver coins to be widely used in ancient times.



*This 1 kg gold nugget was found in Australia; in 2005, it was for sale in Hong Kong at an asking price of more than US$64,000.*

Deposits of gold and copper are widespread and numerous, and for many centuries it was relatively easy to obtain large amounts of the pure elements. For example, a single gold nugget discovered in Australia in 1869 weighed more than 150 lb. Because the demand for these elements has outstripped their availability, methods have been developed to recover them economically from even very low-grade ores (as low as 1% Cu content for copper) by operating on a vast scale, as shown in the photo of an open-pit copper mine. Copper is used primarily to manufacture electric wires, but large quantities are also used to produce bronze, brass, and alloys for coins. Much of the silver made today is obtained as a by-product of the manufacture of other metals, especially Cu, Pb, and Zn. In addition to its use in jewelry and silverware, silver is used in Ag/Zn and Ag/Cd button batteries. Gold is typically found either as tiny particles of the pure metal or as gold telluride ($AuTe_2$). It is used as a currency reserve, in jewelry, in the electronics industry for corrosion-free contacts, and, in very thin layers, as a reflective window coating that minimizes heat transfer.



*The Chuquicamata copper mine in northern Chile, the world's largest open-pit copper mine, is 4.3 km long, 3 km wide, and 825 m deep. Each gigantic truck in the foreground (and barely visible in the lower right center) can hold 330 metric tn (330,000 kg) of copper ore.*

Some properties of the coinage metals are listed in Table 22.2.4. The electronegativity of gold ($\chi$ = 2.40) is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single ns electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au because of the relatively low values of the second and (for Au) third ionization energies. All three elements have significant electron affinities due to the half-filled ns orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold anion $Au^-$ with a $6s^25d^{10}$ valence electron configuration.

Table 22.2.4: Some Properties of the Elements of Groups 11 and 12

| Group | Element | Z | Valence Electron Configuration | Electronegativity | Metallic Radius (pm) | Melting Point (°C) | Density ($g/cm^3$) |
|---|---|---|---|---|---|---|---|
| 11 | Cu | 29 | $4s^13d^{10}$ | 1.90 | 128 | 1085 | 8.96 |
| | Ag | 47 | $5s^14d^{10}$ | 1.93 | 144 | 962 | 10.50 |
| | Au | 79 | $6s^15d^{10}4f^{14}$ | 2.40 | 144 | 1064 | 19.30 |
| 12 | Zn | 30 | $4s^23d^{10}$ | 1.65 | 134 | 420 | 7.13 |
| | Cd | 48 | $5s^24d^{10}$ | 1.69 | 149 | 321 | 8.69 |
| | Hg | 80 | $6s^25d^{10}4f^{14}$ | 1.90 | 151 | −38.8 | 13.53 |

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. Hence they are noble metals that are particularly well suited for use in coins and jewelry. Copper reacts with $O_2$ at high temperatures to produce $Cu_2O$ and with sulfur to form $Cu_2S$. Neither silver nor gold reacts directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black $Ag_2S$ coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidizing acids. Thus both Cu and Ag dissolve in $HNO_3$ and in hot concentrated $H_2SO_4$, while Au dissolves in the 3:1 HCl:$HNO_3$ mixture known as aqua regia. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stable $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores.

> *Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.*

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilize the higher oxidation states ($Au^{3+}$ and $Cu^{2+}$). Thus all the copper(II) halides except the iodide are known, but the only dihalide of silver is $AgF_2$. In contrast, all the gold trihalides ($AuX_3$) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

## Group 12 (Zn, Cd, and Hg)

We next encounter the group 12 elements. Because none of the elements in group 12 has a partially filled (n − 1)d subshell, they are not, strictly speaking, transition metals. Nonetheless, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. Cadmium is used as the cathode in rechargeable NiCad batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process, while smaller amounts are consumed in mercury-vapor streetlights and mercury batteries.

As shown in Table 22.2.4, the group 12 metals are significantly more electropositive than the elements of group 11, and they therefore have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other, but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not. Because mercury, the only metal that is a liquid at room temperature, can dissolve many metals by forming amalgams, medieval alchemists especially valued it when trying to transmute base metals to gold and silver. All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two ns electrons, dominates their chemistry. In addition, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion $Hg_2^{2+}$.

> *The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.*

All the possible group 12 dihalides ($MX_2$) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidizing acids such as $HNO_3$ and $H_2SO_4$. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

### Example 22.2.1

For each reaction, explain why the indicated products form.

a. $TiCl_4(l) + 2H_2O(l) \rightarrow TiO_2(s) + 4HCl(aq)$

b. $WO_3(s) + 3C(s) + 3Cl_2(g) \xrightarrow{\Delta} WCl_6(s) + 3CO(g)$

c. $Sc_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Sc(OH)_4]^-(aq)$

d. $2KMnO_4(aq) + 2H_2SO_4(l) \rightarrow Mn_2O_7(l) + 2KHSO_4(soln) + H_2O(soln)$

e. $4CrCl_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 8Cl^-(aq) + 2H_2O(l)$

**Given**: balanced chemical equation

Asked for: why the indicated products form

**Strategy:**

Refer to the periodic trends in this section.

**Solution**:

a. The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid–base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyze in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.

b. This reaction involves the oxide of a group 6 metal in its highest oxidation state ($WO_3$) and two elements, one of which is a reductant (C) and the other an oxidant ($Cl_2$). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form $CCl_4$, and $WO_3$ is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and chlorine. The most likely combination is $WCl_6$ (leaving the oxidation state of the metal unchanged).

c. One of the reactants is a strong base ($OH^-$), so an acid–base reaction is likely if the other reactant is acidic. Because oxides like $Sc_2O_3$, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect $Sc_2O_3$ to dissolve in base to form a soluble hydroxide complex.

d. Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidized further. A redox reaction is impossible, which leaves an acid–base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.

e. Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidized. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which $Cr^{2+}$ ions are oxidized and $O_2$ is reduced. In the presence of protons, the reduction product of $O_2$ is water, so we need to determine only the identity of the oxidation product of $Cr^{2+}$. Chromium forms compounds in two common higher oxidation states: the $Cr^{3+}$ ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than $O_2$. We therefore predict that the reaction will form $Cr^{3+}(aq)$ and water.

## ? Exercise 22.2.1

Predict the products of each reactions and then balance each chemical equation.

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+}$

b. $Na_2Cr_2O_7(aq) + H_2SO_4(l) \rightarrow$

c. $FeBr_2(aq) + O_2(g) \xrightarrow{H^+}$

d. $VBr_4(l) + H_2O(l) \rightarrow$

e. $ZrO_2(s) + C(s) + Cl_2(g) \xrightarrow{\Delta}$

**Answer**

a. $Cr^{2+}(aq) + Fe^{3+}(aq) \xrightarrow{H^+} Cr^{3+}(aq) + Fe^{2+}(aq)$

b. $Na_2Cr_2O_7(aq) + 2H_2SO_4(l) \rightarrow 2NaHSO_4(soln) + H_2O(soln) + 2CrO_3(s)$

c. $4FeBr_2(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) + 8Br^-(aq)$

d. $VBr_4(l) + H_2O(l) \rightarrow VO^{2+}(aq) + 4Br^-(aq) + 2H^+(aq)$

e. $ZrO_2(s) + 2C(s) + 2Cl_2(g) \xrightarrow{\Delta} ZrCl_4(s) + 2CO(g)$

## Summary

**The elements tend to become more polarizable going across the d block and higher oxidation states become less stable; higher oxidation states become more stable going down a group.** The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form compounds that are largely ionic and with oxygen to form sesquioxides ($M_2O_3$). The group 4 metals also have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-radius ratio causes extensive polarization of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity. The group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states

lower than +5. The oxides are sufficiently polarized to make them covalent in character. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarizable across the row, their affinity for oxygen decreases. The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidizing strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but $Cr_2O_3$ is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups. The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits an extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidizing halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. The group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties. In groups 8, 9, and 10, the ionization potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of group 8 metals in their highest oxidation state are powerful oxidants. The reaction of metals in groups 8, 9, and 10 with the chalcogens is complex, and these elements form a range of binary nitrides, carbides, and borides. The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides. The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

## Contributors and Attributions

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# 22.3: Metallurgy

**Learning Objectives**

- To understand how metals are extracted from their ores.

Very few of the transition metals are found in nature as free metals (e.g., gold and silver). Consequently, almost all metallic elements must be isolated from metal oxide or metal sulfide ores. Metallurgy is the set of processes by which metals are extracted from their ores and converted to more useful forms. Metallurgy consists of three general steps:

1. mining the ore,
2. separating and concentrating the metal or the metal-containing compound, and
3. reducing the ore to the metal.

Additional processes are sometimes required to improve the mechanical properties of the metal or increase its purity. Many ores contain relatively low concentrations of the desired metal; for example, copper ores that contain even 1% Cu by mass are considered commercially useful.

After an ore has been mined, the first step in processing is usually to crush it because the rate of chemical reactions increases dramatically with increased surface area. Next, one of three general strategies is used to separate and concentrate the compound(s) of interest: settling and flotation, which are based on differences in density between the desired compound and impurities; pyrometallurgy, which uses chemical reduction at high temperatures; and hydrometallurgy, which employs chemical or electrochemical reduction of an aqueous solution of the metal. Other methods that take advantage of unusual physical or chemical properties of a particular compound may also be used. For example, crystals of magnetite ($Fe_3O_4$) are tiny but rather powerful magnets; in fact, magnetite (also known as lodestone) was used to make the first compasses in China during the first century BC. If a crushed ore that contains magnetite is passed through a powerful magnet, the $Fe_3O_4$ particles are attracted to the poles of the magnet, allowing them to be easily separated from other minerals.

> Metallurgy depends on the separation of a metal compound from its ore and reduction to the metal at high temperature (pyrometallurgy) or in aqueous solution (hydrometallurgy).

Settling and flotation have been used for thousands of years to separate particles of dense metals such as gold, using the technique known as panning, in which a sample of gravel or sand is swirled in water in a shallow metal pan. Because the density of gold (19.3 $g/cm^3$) is so much greater than that of most silicate minerals (about 2.5 $g/cm^3$), silicate particles settle more slowly and can be poured off with the water, leaving dense gold particles on the bottom of the pan. Conversely, in flotation, the compound of interest is made to float on top of a solution. Blowing air through a suspension of the crude ore in a mixture of water and an organic liquid, such as pine tar, produces a “froth” that contains tiny particles of hydrophobic solids, such as metal sulfides, while more hydrophilic oxide minerals remain suspended in the aqueous phase (Figure 23.3.1). To make the separation more efficient, small amounts of an anionic sulfur-containing compound, such as $Na^+C_2H_5OCS_2^-$, are added; the additive binds to the sulfur-rich surface of the metal sulfide particles and makes the metal sulfide particles even more hydrophobic. The resulting froth is highly enriched in the desired metal sulfide(s), which can be removed simply by skimming. This method works even for compounds as dense as PbS (7.5 $g/cm^3$).

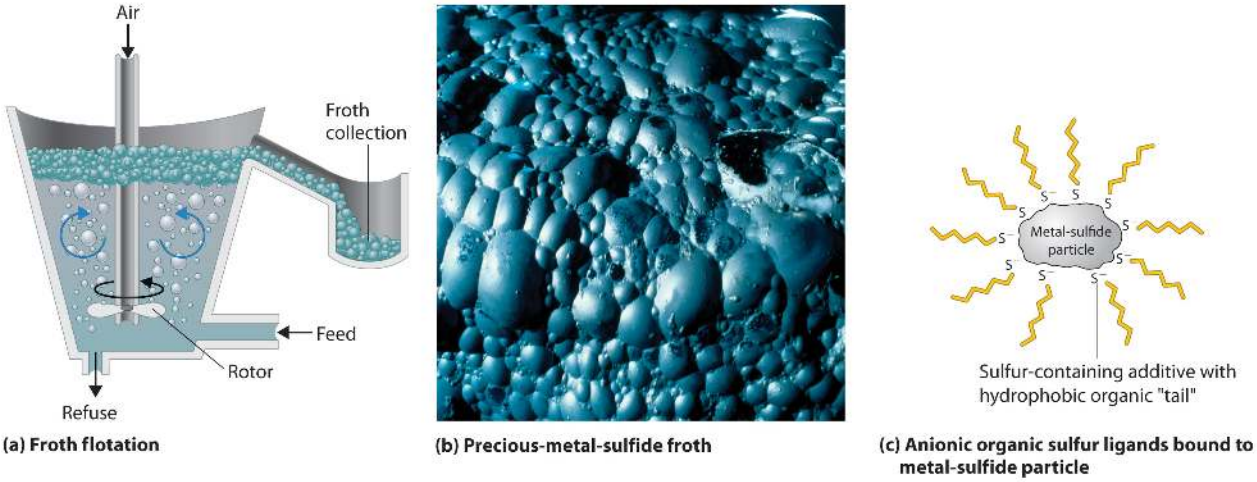



Figure 23.3.1: Froth Flotation. (a) When air is blown through a mixture of a finely ground metal sulfide ore and water, the more hydrophobic metal sulfides form a froth that can be easily removed, allowing them to be separated from more hydrophilic metal oxides and silicates. (b) A froth containing precious metal sulfides is formed as a by-product during the production of metallic nickel. (c) An anionic sulfur additive with hydrophobic “tails” can be used to enhance the hydrophobic character of metal sulfide particles, which causes them to be attracted to the air/water interface in the foam.

## Pyrometallurgy

In pyrometallurgy, an ore is heated with a reductant to obtain the metal. Theoretically, it should be possible to obtain virtually any metal from its ore by using coke, an inexpensive form of crude carbon, as the reductant. An example of such a reaction is as follows:

$$\mathrm{CaO(s) + C(s) \xrightarrow{\Delta} Ca(l) + CO(g)} \tag{23.3.1}$$

Unfortunately, many of the early transition metals, such as Ti, react with carbon to form stable binary carbides. Consequently, more expensive reductants, such as hydrogen, aluminum, magnesium, or calcium, must be used to obtain these metals. Many metals that occur naturally as sulfides can be obtained by heating the sulfide in air, as shown for lead in the following equation:

$$\mathrm{PbS(s) + O_2(g) \xrightarrow{\Delta} Pb(l) + SO_2(g)} \tag{23.3.2}$$

The reaction is driven to completion by the formation of $SO_2$, a stable gas.

Pyrometallurgy is also used in the iron and steel industries. The overall reaction for the production of iron in a blast furnace is as follows:

$$\mathrm{Fe_2O_3(s) + 3C(s) \xrightarrow{\Delta} 2Fe(l) + 3CO(g)} \tag{23.3.3}$$

The actual reductant is CO, which reduces $Fe_2O_3$ to give Fe(l) and $CO_2$(g); the $CO_2$ is then reduced back to CO by reaction with excess carbon. As the ore, lime, and coke drop into the furnace (Figure 23.3.2), any silicate minerals in the ore react with the lime to produce a low-melting mixture of calcium silicates called slag, which floats on top of the molten iron. Molten iron is then allowed to run out the bottom of the furnace, leaving the slag behind. Originally, the iron was collected in pools called pigs, which is the origin of the name pig iron.

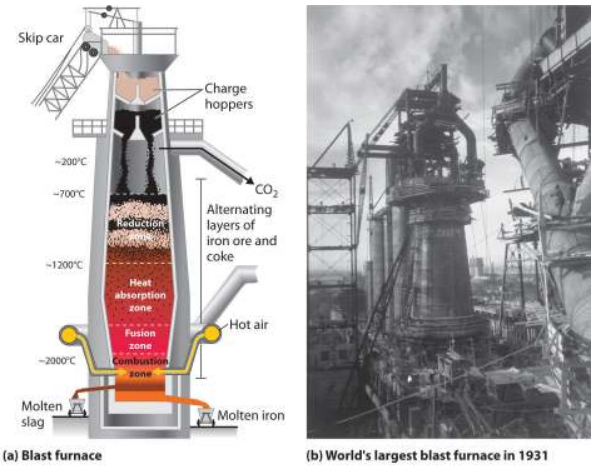



Figure 23.3.2: A Blast Furnace for Converting Iron Oxides to Iron Metal. (a) The furnace is charged with alternating layers of iron ore (largely $Fe_2O_3$) and a mixture of coke (C) and limestone ($CaCO_3$). Blasting hot air into the mixture from the bottom causes it to ignite, producing CO and raising the temperature of the lower part of the blast furnace to about 2000°C. As the CO that is formed initially rises, it reduces $Fe_2O_3$ to form $CO_2$ and elemental iron, which absorbs heat and melts as it falls into the hottest part of the furnace. Decomposition of $CaCO_3$ at high temperatures produces CaO (lime) and additional $CO_2$, which reacts with excess coke to form more CO. (b) This blast furnace in Magnitogorsk, Russia, was the largest in the world when it was built in 1931.

Iron that is obtained directly from a blast furnace has an undesirably low melting point (about 1100°C instead of 1539°C) because it contains a large amount of dissolved carbon. It contains other impurities (such as Si, S, P, and Mn from contaminants in the iron ore that were also reduced during processing) that must be removed because they make iron brittle and unsuitable for most structural applications. In the Bessemer process, oxygen is blown through the molten pig iron to remove the impurities by selective oxidation because these impurities are more readily oxidized than iron (Figure 23.3.3). In the final stage of this process, small amounts of other metals are added at specific temperatures to produce steel with the desired combination of properties.

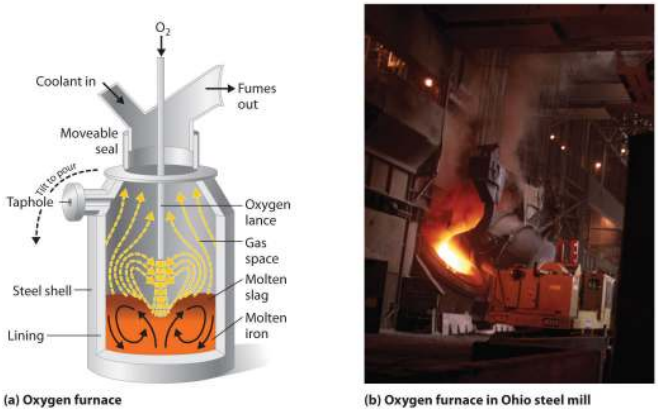



Figure 23.3.3: A Basic Oxygen Furnace for Converting Crude Iron to Steel. (a) A blast of oxygen is used to agitate the molten iron and oxidize impurities to products that dissolve in the less dense slag layer. The slag and the molten steel are removed by tilting the entire furnace and pouring the liquids out through the taphole. (b) A basic oxygen furnace is being filled with molten iron from a blast furnace.

## Hydrometallurgy

The most selective methods for separating metals from their ores are based on the formation of metal complexes. For example, gold is often found as tiny flakes of the metal, usually in association with quartz or pyrite deposits. In those circumstances, gold is typically extracted by using cyanide leaching, which forms a stable gold–cyanide complex—$[Au(CN)_2]^-$:

$$4Au_{(s)} + 8NaCN_{(aq)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 4Na[Au(CN)_2]_{(aq)} + 4NaOH_{(aq)} \tag{23.3.4}$$

Virtually pure gold can be obtained by adding powdered zinc to the solution:

$$Zn_{(s)} + 2[Au(CN)_2]^-_{(aq)} \rightarrow [Zn(CN)_4]^{2-}_{(aq)} + 2Au_{(s)} \tag{23.3.5}$$

A related method, which is used to separate $Co^{3+}$, $Ni^{2+}$, and $Cu^{+}$ from Fe, Mn, and Ti, is based on the formation of stable, soluble ammonia complexes of ions of the late transition metals.

### Example 23.3.1

Suppose you are working in the chemistry laboratory of a mining company that has discovered a new source of tungsten ore containing about 5% $WS_2$ in a granite matrix (granite is a complex aluminosilicate mineral). You have been asked to outline an economical procedure for isolating $WS_2$ from the ore and then converting it to elemental tungsten in as few steps as possible. What would you recommend?

**Given**: composition of ore

Asked for: procedure to isolate metal sulfide

**Strategy:**

Determine which method would be most effective for separating the metal sulfide from the ore. Then determine the best method for reducing the metal to the pure element.

**Solution**

You need to separate and concentrate the $WS_2$, convert it to a suitable form so it can be reduced to the metal (if necessary), and then carry out the reduction. Because the new ore is a binary metal sulfide, you could take advantage of the hydrophilic nature of most metal sulfides to separate $WS_2$ by froth flotation. Then, because most metal sulfides cannot be reduced directly to the metal using carbon, you will probably need to convert $WS_2$ to an oxide for subsequent reduction. One point to consider is whether the oxide can be reduced using carbon because many transition metals react with carbon to form stable carbides. Here is one possible procedure for producing tungsten from this new ore:

1. Grind the ore and separate $WS_2$ from the silicate matrix by flotation.
2. Convert the crude $WS_2$ to an oxide by roasting in air (because W is in group 6, you anticipate that roasting will yield $WO_3$, the oxide in the highest possible oxidation state). The reaction will also produce $SO_2$, which will have to be removed by scrubbing the exhaust gases to minimize environmental pollution.
3. Reduce the oxide with hydrogen gas at high temperature to avoid carbide formation:

$$WO_3(s) + 3H_2(g) \xrightarrow{\Delta} W(s) + 3H_2O(g)$$

### Exercise 23.3.1

Propose an economical procedure for converting a silicate mineral deposit containing $BaCO_3$ to the pure Ba metal.

**Answer**:

1. Dissolve the sample containing barium carbonate in HCl(aq) to give $Ba^{2+}$(aq), which will allow the insoluble silicate minerals to be removed by filtration.
2. Precipitate the barium from solution as $BaCO_3$ by adding solid $Na_2CO_3$.
3. Dissolve the solid $BaCO_3$ in concentrated HCl and remove the water by evaporation to obtain anhydrous $BaCl_2$.
4. Reduce molten $BaCl_2$ to the metal by electrolysis.

## Summary

- A metal is separated from its ore and then isolated by using pyrometallurgy or hydrometallurgy or by taking advantage of unusual chemical or physical properties of a particular compound.

The conversion of metals from their ores to more useful forms is called metallurgy, which consists of three general steps: mining, separation and concentration, and reduction. Settling and flotation are separation methods based on differences in density, whereas pyrometallurgy is based on a chemical reduction at elevated temperatures, and hydrometallurgy uses chemical or electrochemical reduction of an aqueous solution. In pyrometallurgy, a reductant must be used that does not form stable compounds with the metal of interest. In hydrometallurgy, metals are separated via the formation of metal complexes.

## Conceptual Problems

1. Coke is a plentiful and inexpensive reductant that is used to isolate metals from their ores. Of Cr, Co, W, Cu, Ni, Os, Fe, Mn, La, and Hf, which cannot be isolated using this reductant? Why?
2. Hydrometallurgy is the preferred method for separating late transition metals from their ores. What types of ligands are most effective in this process?

## Answer

1. Coke cannot be used as a reductant for metals that form stable carbides, such as the early transition metals (La, Hf, and W).

## Structure and Reactivity

1. Tantalum and niobium are frequently found together in ores. These elements can be separated from other metals present by treatment with a solution of HF. Explain why this is an effective separation technique.
2. A commercially important ore of chromium is chromite ($FeCr_2O_4$), which is an analogue of magnetite ($Fe_3O_4$). Based on what you know about the oxidation states of iron in magnetite, predict the oxidation states of the metal ions in chromite.
3. Pure vanadium is obtained by reducing $VCl_4$ with $H_2$ or Mg or by reducing $V_2O_5$ with Ca. Write a balanced chemical equation for each reaction. Why is carbon not used for the reduction?
4. Manganese is an important additive in steel because of its reactivity with oxygen and sulfur, both of which contribute to brittleness. Predict the products of reacting Mn with these species.
5. The diagram of a blast furnace in Figure 23.3.2 illustrates several important features of the reduction of $Fe_2O_3$ to iron. Write a balanced chemical equation for each step of the process described in the figure and give the overall equation for the conversion. Oxygen is blown through the final product to remove impurities. Why does this step not simply reverse the process and produce iron oxides?
6. Metallic Zr is produced by the Kroll method, which uses Na as the reductant. Write a balanced chemical equation for each reaction involved in this process. The product is frequently contaminated with Hf. Propose a feasible method for separating the two elements.
7. The compound $Cr_2O_3$ is important commercially; among other things, it is used as a pigment in paint and as a catalyst for the manufacture of butadiene. Write a balanced chemical equation to show how you would produce this compound from

    a. chromium metal.
    b. ammonium dichromate.
    c. $CrCl_3$ in a basic solution.

## Answer

3.

$$VCl_4(l) + 2H_2(g) \xrightarrow{\Delta} V(s) + 4HCl(g) \tag{22.3.1}$$

$$VCl_4(l) + 2Mg(s) \xrightarrow{\Delta} V(s) + 2MgCl_2(g) \tag{22.3.2}$$

$$V_2O_5(s) + 5Ca(s) \xrightarrow{\Delta} 2V(s) + 5CaO(s) \tag{22.3.3}$$

Carbon cannot be used as a reductant because vanadium forms stable carbides, such as VC and $VC_2$.

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# 22.4: Coordination Compounds

**Learning Objectives**

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands.

One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A **metal complex** consists of a central metal atom or ion that is bonded to one or more **ligands** (from the Latin *ligare*, meaning “to bind”), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called **complex ions**. A **coordination compound** contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions. Metal complexes are so important in biology that we consider the topic separately in Section 23.6.

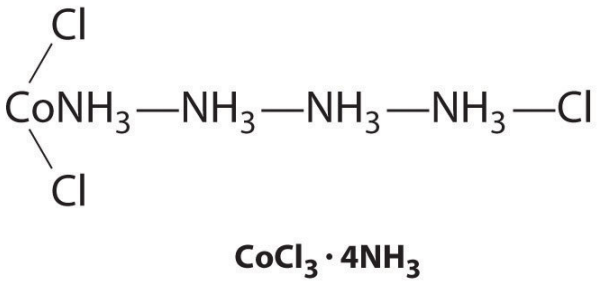
## History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called “double salts” were known, such as $AlF_3{\cdot}3KF$, $Fe(CN)_2{\cdot}4KCN$, and $ZnCl_2{\cdot}2CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3{\cdot}3KF$ exist but not $AlF_3{\cdot}4KF$ or $AlF_3{\cdot}2KF$? And why should a 3:1 KF:$AlF_3$ mixture have different chemical and physical properties than either of its components? Similarly, *adducts* of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3{\cdot}6NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3{\cdot}6NH_3$, $CoCl_3{\cdot}5NH_3$, $CoCl_3{\cdot}4NH_3$, and $CoCl_3{\cdot}3NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3{\cdot}2NH_3$ or $CoCl_3{\cdot}NH_3$.



***The Great Wave Off Kanagawa.*** *The Japanese artist Katsushika Hokusai used Prussian blue to create this famous woodcut.*

Although the chemical *composition* of such compounds was readily established by existing analytical methods, their chemical *nature* was puzzling and highly controversial. The major problem was that what we now call *valence* (i.e., the oxidation state) and *coordination number* were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the "Chattanooga choo-choo" model for $CoCl_3 \cdot 4NH_3$ shown here.




The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4 \cdot nNH_3$ ($n$ = 2–6). Some of Werner's original data on these compounds are shown in Table 22.4.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of "free" chloride ions present. For example, Werner's data on $PtCl_4 \cdot 6NH_3$ in Table 22.4.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4 \cdot 2NH_3$ was a neutral molecule that contained no free chloride ions.

### Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 22.4.1 Werner's Data on Complexes of Ammonia with $PtCl_4$

| Complex | Conductivity ($ohm^{-1}$) | Number of Ions per Formula Unit | Number of $Cl^-$ Ions Precipitated by $Ag^+$ |
|---|---|---|---|
| $PtCl_4 \cdot 6NH_3$ | 523 | 5 | 4 |
| $PtCl_4 \cdot 5NH_3$ | 404 | 4 | 3 |
| $PtCl_4 \cdot 4NH_3$ | 299 | 3 | 2 |
| $PtCl_4 \cdot 3NH_3$ | 97 | 2 | 1 |
| $PtCl_4 \cdot 2NH_3$ | 0 | 0 | 0 |

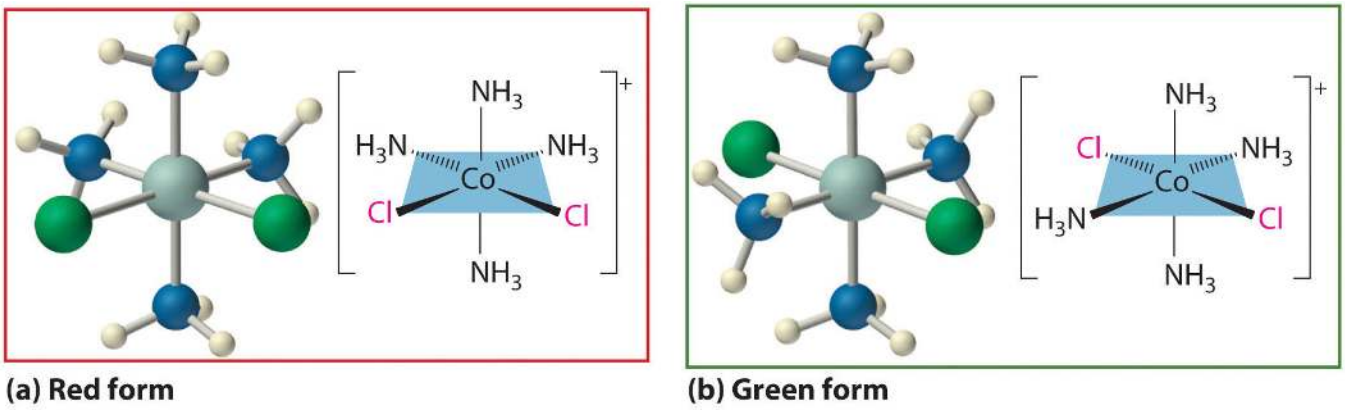
These data led Werner to postulate that metal ions have two different kinds of valence: (1) a *primary valence* (oxidation state) that corresponds to the positive charge on the metal ion and (2) a *secondary valence* (coordination number) that is the total number of ligands bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$\begin{aligned}
[\mathrm{Pt(NH_3)_6}]\,\mathrm{Cl_4} &\rightarrow [\mathrm{Pt(NH_3)_6}]^{4+}(\mathrm{aq}) + 4\mathrm{Cl^-}(\mathrm{aq}) \\
[\mathrm{Pt(NH_3)_5\,Cl}]\,\mathrm{Cl_3} &\rightarrow [\mathrm{Pt(NH_3)_5\,Cl}]^{3+}(\mathrm{aq}) + 3\mathrm{Cl^-}(\mathrm{aq}) \\
[\mathrm{Pt(NH_3)_4\,Cl_2}]\,\mathrm{Cl_2} &\rightarrow [\mathrm{Pt(NH_3)_4\,Cl_2}]^{2+}(\mathrm{aq}) + 2\mathrm{Cl^-}(\mathrm{aq}) \\
[\mathrm{Pt(NH_3)_3\,Cl_3}]\,\mathrm{Cl} &\rightarrow [\mathrm{Pt(NH_3)_3\,Cl_3}]^{+}(\mathrm{aq}) + \mathrm{Cl^-}(\mathrm{aq}) \\
[\mathrm{Pt(NH_3)_2\,Cl_4}] &\rightarrow [\mathrm{Pt(NH_3)_2\,Cl_4}]^{0}(\mathrm{aq})
\end{aligned} \tag{22.4.1}$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for $Co^{3+}$ and $Cr^{3+}$ and 4 for $Pt^{2+}$ and $Pd^{2+}$.

Werner's studies on the analogous $Co^{3+}$ complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (part (a) in Figure 22.4.1. Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the *arrangement* of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (part (b) in Figure 22.4.1. His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

Figure 22.4.1 *Complexes with Different Arrangements of the Same Ligands Have Different Properties*




*The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two $Cl^-$ ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).*

### Example 22.4.1

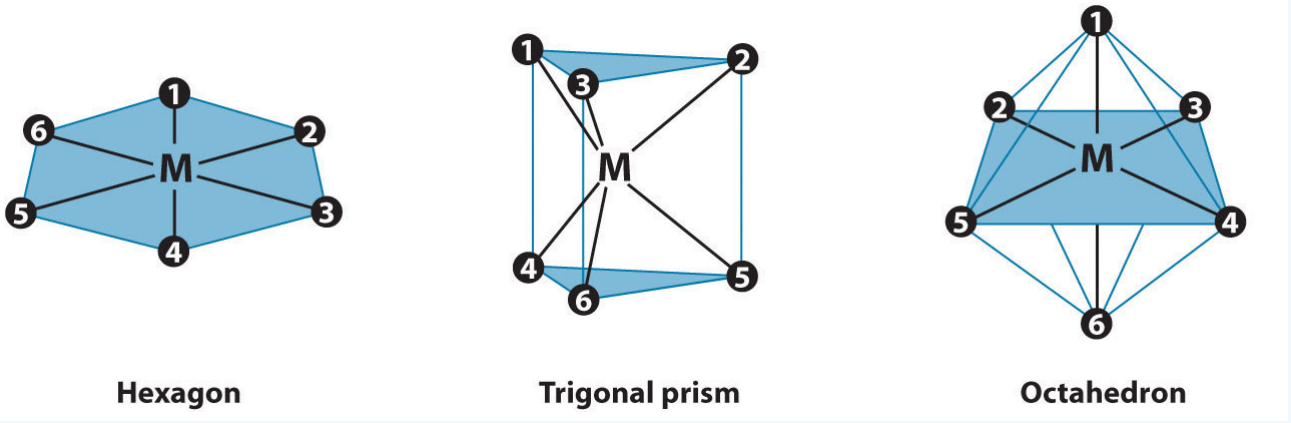
In Werner's time, many complexes of the general formula $MA_4B_2$ were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate $MA_4B_2$ complexes with each of the three

**Given:** three possible structures and the number of different forms known for $MA_4B_2$ complexes

**Asked for:** number of different arrangements of ligands for $MA_4B_2$ complex for each structure

**Solution**

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical $MA_6$ complex and simply replace two of the A ligands in each structure to give an $MA_4B_2$ complex:




For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible $MA_4B_2$ arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all $MA_4B_2$ complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., $MA_3B_3$), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

**? Exercise 22.4.1**

Determine the maximum number of structures that are possible for a four-coordinate $MA_2B_2$ complex with either a square planar or a tetrahedral symmetrical structure.

**Answer**

square planar, 2; tetrahedral, 1

## Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model in Chapter 9 because they correspond to the lowest-energy arrangements of $n$ electron pairs around a central atom.

### Note the Pattern

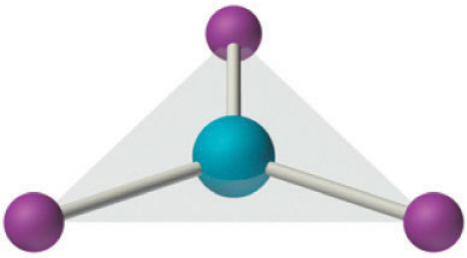
Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.

## Coordination Number 2




Although it is rare for most metals, this coordination number is surprisingly common for $d^{10}$ metal ions, especially $Cu^+$, $Ag^+$, $Au^+$, and $Hg^{2+}$. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores, as described in Section 23.3. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.

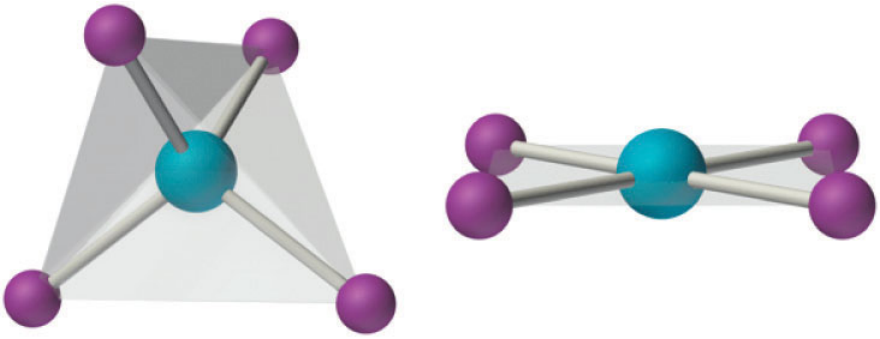
## Coordination Number 3



Trigonal planar $ML_3$

Although it is also rare, this coordination number is encountered with $d^{10}$ metal ions such as $Cu^+$ and $Hg^{2+}$. Among the few known examples is the $HgI_3^-$ ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.

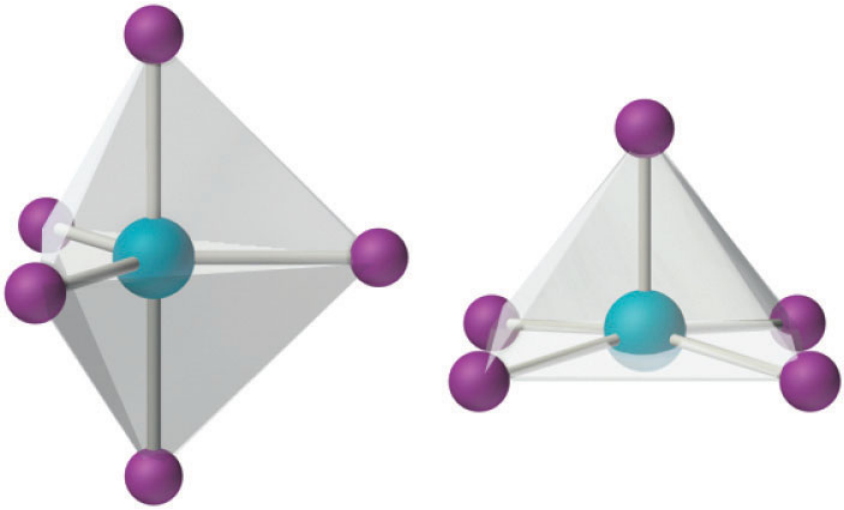
## Coordination Number 4



Tetrahedral and square planar $ML_4$

Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and $d^{10}$ ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with $d^8$ electron configurations, such as $Rh^+$ and $Pd^{2+}$, and they are also encountered in some complexes of $Ni^{2+}$ and $Cu^{2+}$.

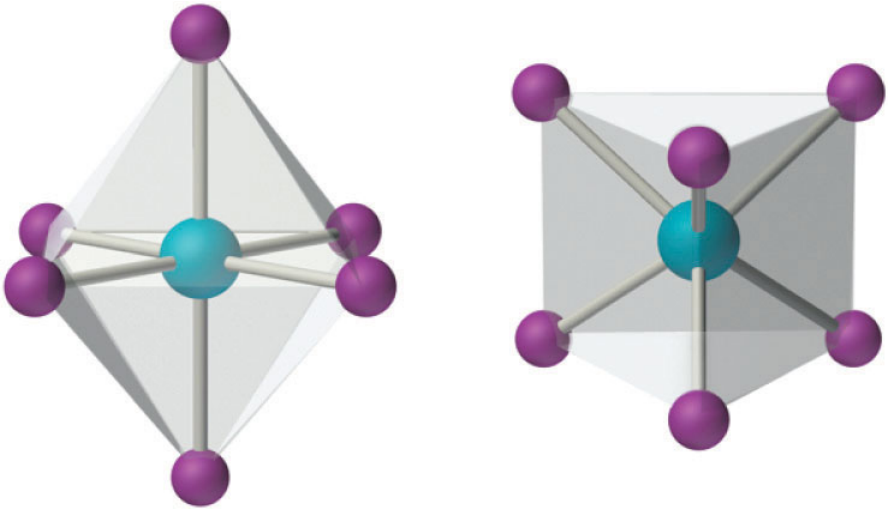
## Coordination Number 5



Trigonal bipyramidal and square pyramidal $ML_5$

This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.

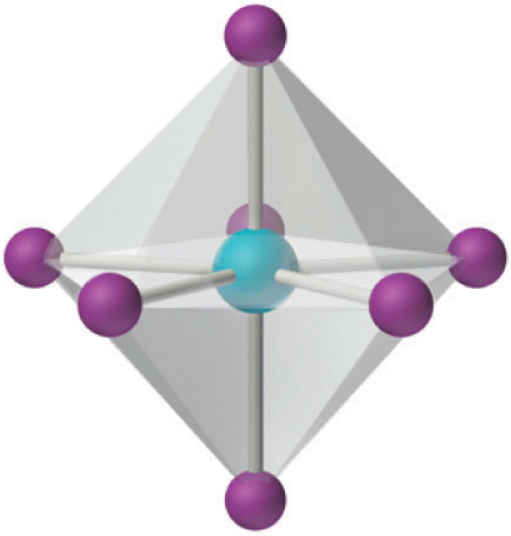
## Coordination Number 6



Octahedral and trigonal prismatic $ML_6$

This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.

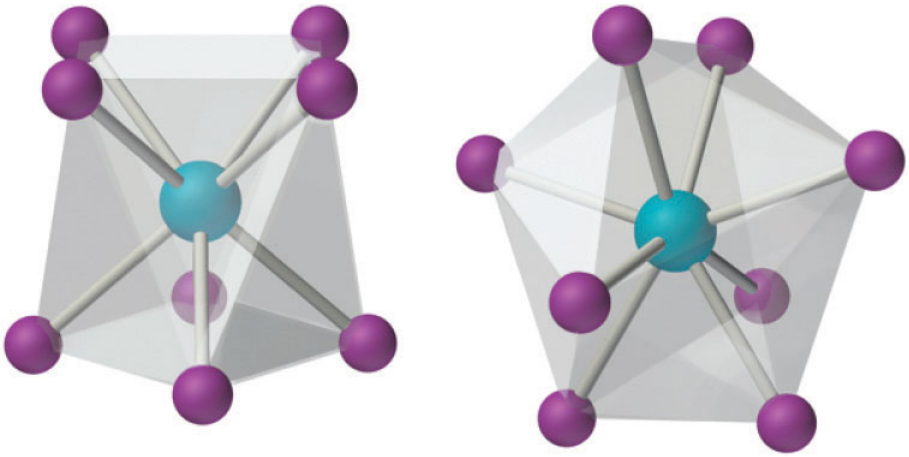
## Coordination Number 7



Pentagonal bipyramidal $ML_7$

This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.

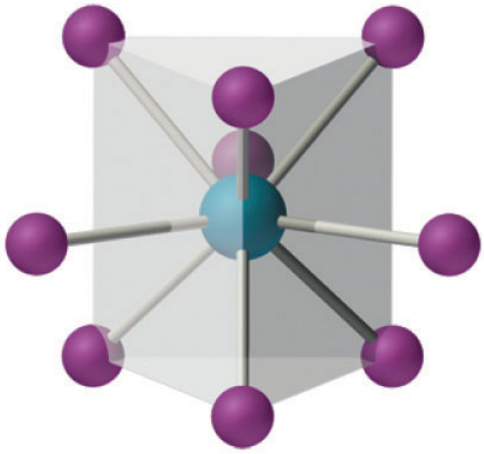
## Coordination Number 8



Square antiprismatic and trigonal dodecahedral $ML_8$

This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.

## Coordination Number 9



# Tricapped trigonal prismatic $ML_9$

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.

## Stability of Metal Complexes

The thermodynamic stability of a metal complex depends greatly on the properties of the ligand and the metal ion and on the type of bonding. Recall that the metal–ligand interaction is an example of a Lewis acid–base interaction. Lewis bases can be divided into two categories: **hard bases**, which contain small, relatively nonpolarizable donor atoms (such as N, O, and F), and **soft bases**, which contain larger, relatively polarizable donor atoms (such as P, S, and Cl). Metal ions with the highest affinities for hard bases are **hard acids**, whereas metal ions with the highest affinity for soft bases are **soft acids**. Some examples of hard and soft acids and bases are given in Table 22.4.2. Notice that hard acids are usually cations of electropositive metals; consequently, they are relatively nonpolarizable and have higher charge-to-radius ratios. Conversely, soft acids tend to be cations of less electropositive metals; consequently, they have lower charge-to-radius ratios and are more polarizable. Chemists can predict the relative stabilities of complexes formed by the *d*-block metals with a remarkable degree of accuracy by using a simple rule: *hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases*.

Table 22.4.2 Examples of Hard and Soft Acids and Bases

| | Acids | Bases |
|---|---|---|
| hard | $H^+$ | $NH_3$, $RNH_2$, $N_2H_4$ |
| | $Li^+$, $Na^+$, $K^+$ | $H_2O$, ROH, $R_2O$ |
| | $Be^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $VO^{2+}$ | $OH^-$, $F^-$, $Cl^-$, $CH_3CO_2^-$ |
| | $Al^{3+}$, $Sc^{3+}$, $Cr^{3+}$ | $CO_3^{2-}$ |
| | $Ti^{4+}$ | $PO_4^{3-}$ |
| soft | $BF_3$, $Al_2Cl_6$, $CO_2$, $SO_3$ | |
| | $Cu^+$, $Ag^+$, $Au^+$, $Tl^+$, $Hg_2^{2+}$ | $H^-$ |
| | $Pd^{2+}$, $Pt^{2+}$, $Hg^{2+}$ | $CN^-$, $SCN^-$, $I^-$, $RS^-$ |
| | $GaCl_3$, $GaBr_3$, $GaI_3$ | CO, $R_2S$ |

Because the interaction between hard acids and hard bases is primarily electrostatic in nature, the stability of complexes involving hard acids and hard bases increases as the positive charge on the metal ion increases and as its radius decreases. For example, the complex of $Al^{3+}$ ($r$ = 53.5 pm) with four fluoride ligands ($AlF_4^-$) is about $10^8$ times more stable than $InF_4^-$, the corresponding fluoride complex of $In^{3+}$ ($r$ = 80 pm). In general, the stability of complexes of divalent first-row transition metals with a given ligand varies inversely with the radius of the metal ion, as shown in the following series:The inversion in the order at copper is due to the anomalous structure of copper(II) complexes, which will be discussed shortly.

$$\begin{array}{l} \text{complex stability } Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+} \\ 78 \quad 74.5 \\ 69 \\ 73 \quad 74 \\ \text{ionic radius (pm)} \quad 83 \quad 7 \\ 6 \\ - \end{array} \tag{22.4.2}$$

Because a hard metal interacts with a base in much the same way as a proton, by binding to a lone pair of electrons on the base, the stability of complexes of hard acids with hard bases increases as the ligand becomes more basic. For example, because ammonia is a stronger base than water, metal ions bind preferentially to ammonia. Consequently, adding ammonia to aqueous solutions of many of the first-row transition-metal cations results in the formation of the corresponding ammonia complexes.

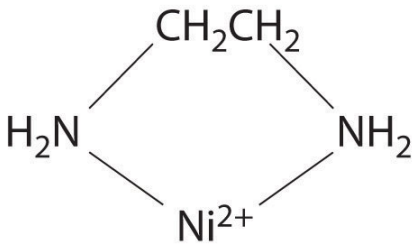
In contrast, the interaction between soft metals (such as the second- and third-row transition metals and $Cu^+$) and soft bases is largely covalent in nature. Most soft-metal ions have a filled or nearly filled *d* subshell, which suggests that metal-to-ligand π bonding is important. Complexes of soft metals with soft bases are therefore much more stable than would be predicted based on electrostatic arguments.

### Note the Pattern

Hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.

The hard acid–hard base/soft acid–soft base concept also allows us to understand why metals are found in nature in different kinds of ores. Recall from Section 23.2 that most of the first-row transition metals are isolated from oxide ores but that copper and zinc tend to occur naturally in sulfide ores. This is consistent with the increase in the soft character of the metals across the first row of the transition metals from left to right. Recall also that most of the second- and third-row transition metals occur in nature as sulfide ores, consistent with their greater soft character.

Ligands like chloride, water, and ammonia are said to be *monodentate* (one-toothed, from the Greek *mono*, meaning “one,” and the Latin *dent-*, meaning “tooth”): they are attached to the metal via only a single atom. Ligands can, however, be *bidentate* (two-toothed, from the Greek *di*, meaning “two”), *tridentate* (three-toothed, from the Greek *tri*, meaning “three”), or, in general, *polydentate* (many-toothed, from the Greek *poly*, meaning “many”), indicating that they are attached to the metal at two, three, or several sites, respectively. Ethylenediamine ($H_2NCH_2CH_2NH_2$, often abbreviated as en) and diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, often abbreviated as dien) are examples of a bidentate and a tridentate ligand, respectively, because each nitrogen atom has a lone pair that can be shared with a metal ion. When a bidentate ligand such as ethylenediamine binds to a metal such as $Ni^{2+}$, a five-membered ring is formed. A metal-containing ring like that shown is called a *chelate* ring (from the Greek *chele*, meaning “claw”). Correspondingly, a polydentate ligand is a *chelating agent*, and complexes that contain polydentate ligands are called *chelate complexes*.




**A chelate complex**

Experimentally, it is observed that metal complexes of polydentate ligands are significantly more stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the **chelate effect**. For example, the complex of $Ni^{2+}$ with three ethylenediamine ligands, $[Ni(en)_3]^{2+}$, should be chemically similar to the $Ni^{2+}$ complex with six ammonia ligands, $[Ni(NH_3)_6]^{2+}$. In fact, the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ is almost 10 orders of magnitude larger than the equilibrium constant for the formation of $[Ni(NH_3)_6]^{2+}$:

$$\begin{aligned} [\mathrm{Ni}\,(\mathrm{H_2O})_6]^{2+} + 6\mathrm{NH_3} &\rightleftharpoons [\mathrm{Ni}\,(\mathrm{NH_3})_6]^{2+} + 6\mathrm{H_2O(l)} \quad K_\mathrm{f} = 4 \times 10^8 \\ [\mathrm{Ni}\,(\mathrm{H_2O})_6]^{2+} + 3\mathrm{en} &\rightleftharpoons [\mathrm{Ni}\,(\mathrm{NH_3})_6]^{2+} + 6\mathrm{H_2O(l)} \quad K_\mathrm{f} = 2 \times 10^{18} \end{aligned} \tag{22.4.3}$$

### Note the Pattern

Chelate complexes are more stable than the analogous complexes with monodentate ligands.

The stability of a chelate complex depends on the *size* of the chelate rings. For ligands with a flexible organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings, which are in turn much more stable than complexes with four- or seven-membered rings. For example, the complex of copper(II) with two ethylenediamine ligands is about 1000 times more stable than the corresponding complex with triethylenediamine ($H_2NCH_2CH_2CH_2NH_2$, abbreviated as trien):

$$\begin{aligned} [\mathrm{Cu}\,(\mathrm{H_2O})_6]^{2+} + 2\mathrm{en} &\rightleftharpoons [\mathrm{Cu(en)_2}]^{2+} + 6\mathrm{H_2O(l)} \quad K_\mathrm{f} = 10^{20} \\ [\mathrm{Cu}\,(\mathrm{H_2O})_6]^{2+} + 3\ \mathrm{trien} &\rightleftharpoons [\mathrm{Cu(\ trien\ )_2}]^{2+} + 6\mathrm{H_2O(l)} \quad K_\mathrm{f} = 10^{17} \end{aligned}$$

**Example 22.4.2**

Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

**Given:** four Cr(III) complexes

**Asked for:** relative stabilities

**Solution**

**A** Determine the relative basicity of the ligands to identify the most stable complexes.

**B** Decide whether any complexes are further stabilized by a chelate effect and arrange the complexes in order of increasing stability.

**Solution:**

**A** The metal ion is the same in each case: $Cr^{3+}$. Consequently, we must focus on the properties of the ligands to determine the stabilities of the complexes. Because the stability of a metal complex increases as the basicity of the ligands increases, we need to determine the relative basicity of the four ligands. Our earlier discussion of acid–base properties suggests that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability expected due to ligand basicity is $[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}$.

**B** Because of the chelate effect, we expect ethylenediamine to form a stronger complex with $Cr^{3+}$ than ammonia. Consequently, the likely order of increasing stability is $[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}$.

**? Exercise 22.4.2**

Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

**Answer**

$[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

## Isomers of Metal Complexes

As we discussed earlier in this section, the existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall from Chapter 2 that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include *n*-butane versus isobutane and *cis*-2-butene versus *trans*-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique. (For more information on isomers in organic compounds, see Chapter 24, Section 24.2.)

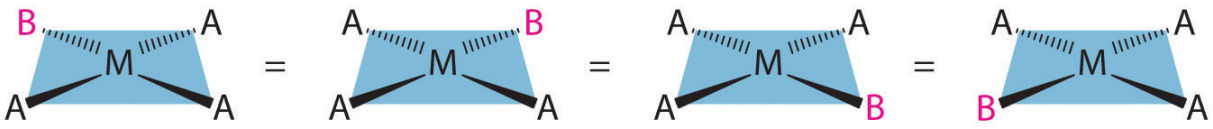
## Structural Isomers

Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called **structural isomers**. Isobutane and *n*-butane are examples of structural isomers. One kind of isomerism consists of two compounds that have the same empirical formula but differ in the number of formula units present in the molecular formula. An example in coordination compounds is two compounds with the empirical formula $Pt(NH_3)_2Cl_2$. One is a simple square planar platinum(II) complex, $Pt(NH_3)_2Cl_2$, and the other is an ionic compound that contains the $[Pt(NH_3)_4]^{2+}$ cation and the $[PtCl_4]^{2-}$ anion, $[Pt(NH_3)_4][PtCl_4]$. As you might expect, these compounds have very different physical and chemical properties. One arrangement of the $Cl^-$ and $NH_3$ ligands around the platinum ion in the former gives the anticancer drug cisplatin, whereas the other arrangement has no known biomedical applications.

## Geometrical Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called **geometrical isomers**. They are most important for square planar and octahedral complexes.

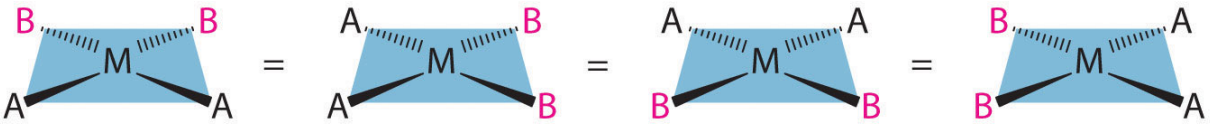
Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar $MA_3B$ complex; hence only a single geometrical isomer is possible in this case (and in the analogous $MAB_3$ case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



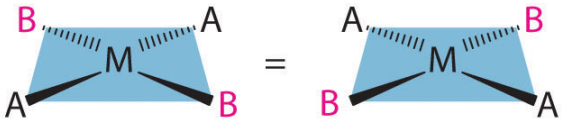

**$MA_3B$ square planar complex**

For an $MA_2B_2$ complex, there are two possible isomers: either the A ligands can be adjacent to one another (*cis*), in which case the B ligands must also be *cis*, or the A ligands can be across from one another (*trans*), in which case the B ligands must also be *trans*.

Even though it is possible to draw the *cis* isomer in four different ways and the *trans* isomer in two different ways, all members of each set are chemically equivalent:

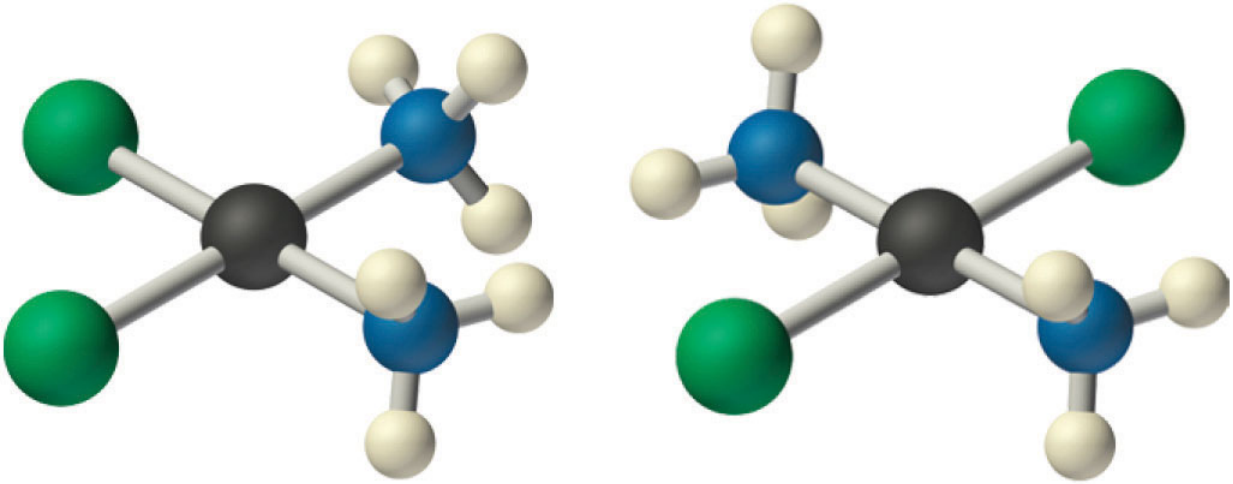



**$MA_2B_2$ square planar complex, *cis* isomer**



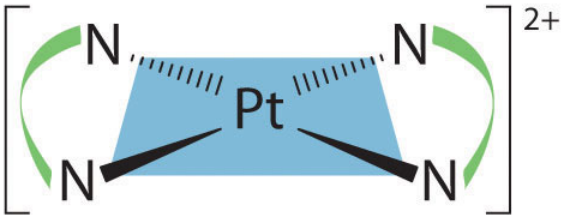

**$MA_2B_2$ square planar complex, *trans* isomer**

Because there is no way to convert the *cis* structure to the *trans* by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of *cis* and *trans* isomers of an $MA_2B_2$ square planar complex are *cis*-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and *trans*-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



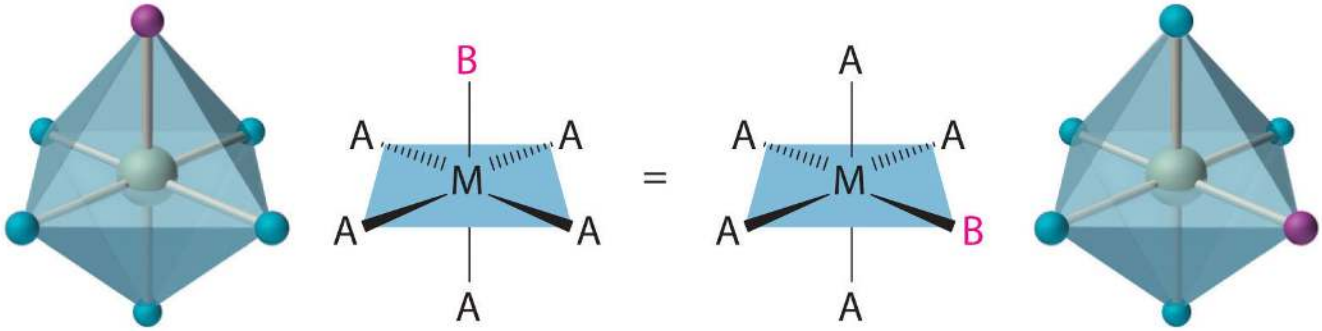

***The anticancer drug cisplatin and its inactive* trans *isomer.*** *Cisplatin is especially effective against tumors of the reproductive organs (the testes in males and the ovaries in females), which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin and went on to win an unprecedented seven Tour de France bicycle races.*

Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



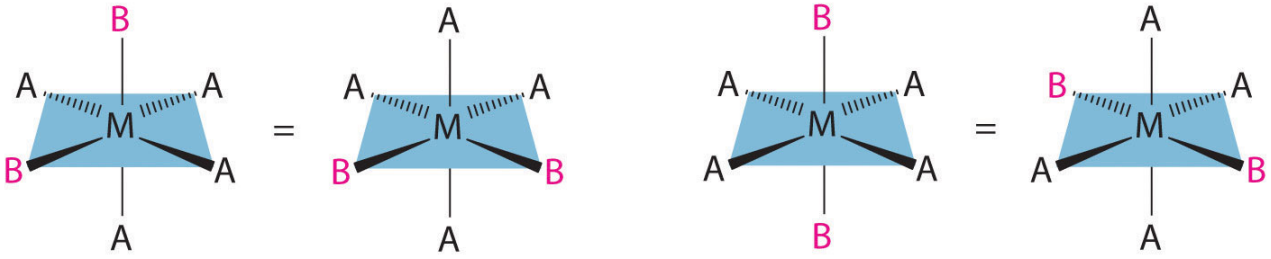

$[Pt(en)_2]^{2+}$

Octahedral complexes also exhibit *cis* and *trans* isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five ($MA_5B$). Even though we usually draw an octahedron in a way that suggests that the four "in-plane" ligands are different from the two "axial" ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an $MA_5B$ structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an $MA_5B$ structure are as follows:




**$MA_5B$ octahedral complex**

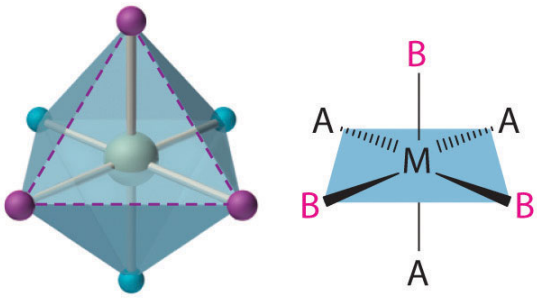
If two ligands in an octahedral complex are different from the other four, giving an $MA_4B_2$ complex, two isomers are possible. The two B ligands can be *cis* or *trans*. *Cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



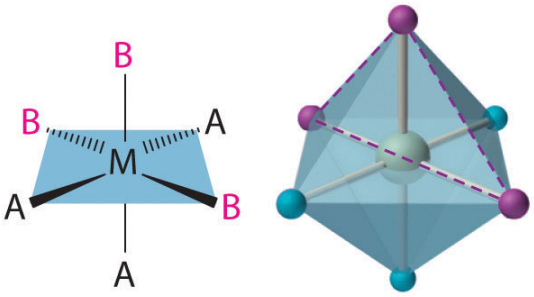

**$MA_4B_2$ octahedral complex, *cis* isomer**

**$MA_4B_2$ octahedral complex, *trans* isomer**

Replacing another A ligand by B gives an $MA_3B_3$ complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the **fac** isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the **mer** isomer (for meridional):




$MA_3B_3$ octahedral complex, *fac* isomer




$MA_3B_3$ octahedral complex, *mer* isomer

## Example 22.4.1

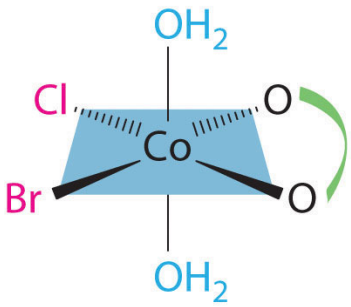
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

**Given:** formula of complex

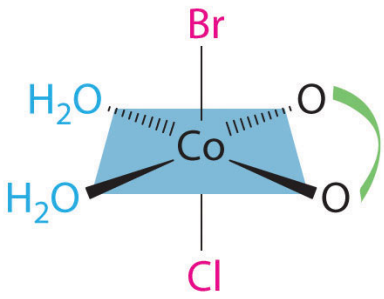
**Asked for:** structures of geometrical isomers

**Solution:**

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical ($H_2O$). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be *trans*. Thus either the water ligands can be *trans* to one another or the two halide ligands can be *trans* to one another, giving the two geometrical isomers shown here:

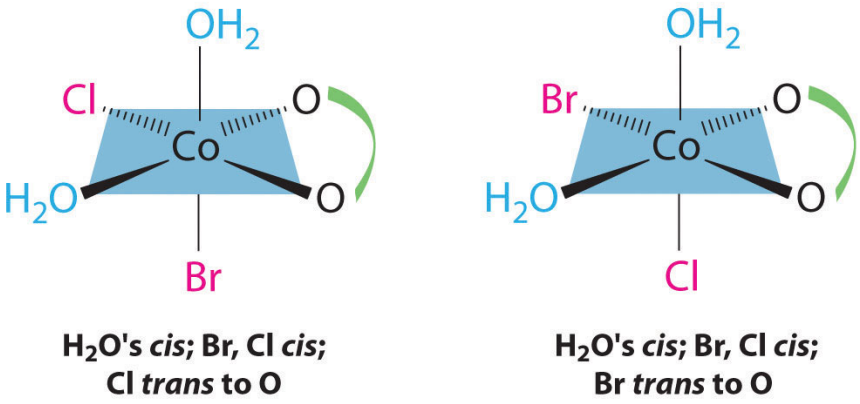



$H_2O$'s *trans*




Br, Cl *trans*

In addition, two structures are possible in which one of the halides is *trans* to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and *trans* to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and *trans* to one of the oxalate oxygens:

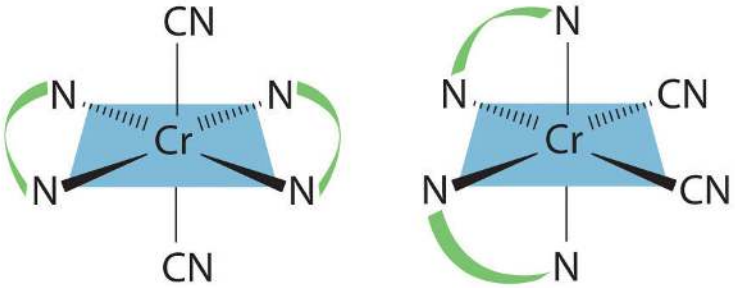



This complex can therefore exist as four different geometrical isomers.

**? Exercise 22.4.1**

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

**Answer**




Two geometrical isomers are possible: *trans* and *cis*.

## Summary

Transition metals form **metal complexes**, polyatomic species in which a metal ion is bound to one or more **ligands**, which are groups bound to a metal ion. **Complex ions** are electrically charged metal complexes, and a **coordination compound** contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for $d^{10}$ metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions. The stability of metal complexes with first-row transition metals in a +2 oxidation state varies inversely with their ionic radius. Lewis bases can be **hard bases**, which have small, relatively nonpolarizable donor atoms, or **soft bases**, with larger, relatively polarizable donor atoms. **Hard acids** have the highest affinity for hard bases, and **soft acids** have the highest affinity for soft bases. Soft metals and soft bases form complexes that are more stable than would be predicted based on electrostatic arguments, which suggests that metal-to-ligand π bonding is important. Ligands that are strong bases form the most stable complexes with metal ions that are hard acids. Exceptionally stable complexes are formed by chelates, which are polyatomic ligands with two or more donor atoms; this enhanced stability is known as the chelate effect. Many metal complexes form **isomers**, which are two or more compounds with the same formula but different arrangements of atoms. **Structural isomers** differ in which atoms are bonded to one another, while **geometrical isomers** differ

only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are **cis**, while ligands across from one another are **trans**.

## KEY TAKEAWAYS

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

## CONCEPTUAL PROBLEMS

1. Give two reasons a metal can bind to only a finite number of ligands. Based on this reasoning, what do you predict is the maximum coordination number of Ti? of Ac?
2. Can a tetrahedral $MA_2B_2$ complex form *cis* and *trans* isomers? Explain your answer.
3. The group 12 elements are never found in their native (free) form but always in combination with one other element. What element is this? Why? Which of the group 12 elements has the highest affinity for the element you selected?

### Answer

1.
2.
3. The group 12 metals are rather soft and prefer to bind to a soft anion such as sulfide rather than to a hard anion like oxide; hence they are usually found in nature as sulfide ores. Because it is the softest of these metals, mercury has the highest affinity for sulfide.

## STRUCTURE AND REACTIVITY

1. Complexes of metals in the +6 oxidation state usually contain bonds to which two Lewis bases? Why are these bonds best described as covalent rather than ionic? Do Ca, Sr, and Ba also form covalent bonds with these two Lewis bases, or is their bonding best described as ionic?
2. Cr, Mn, Fe, Co, and Ni form stable CO complexes. In contrast, the earlier transition metals do not form similar stable complexes. Why?
3. The transition metals Cr through Ni form very stable cyanide complexes. Why are these complexes so much more stable than similar compounds formed from the early transition metals?
4. Of $Co(en)_3^{3+}$, $CoF_6^{3-}$, $Co(NH_3)_6^{3+}$, and $Co(dien)_2^{3+}$, which species do you expect to be the most stable? Why?
5. Of $Ca^{2+}$, $Ti^{2+}$, $V^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Zn^{2+}$, which divalent metal ions forms the most stable complexes with ligands such as $NH_3$? Why?
6. Match each Lewis base with the metal ions with which it is most likely to form a stable complex:

   Lewis bases: $NH_3$, $F^-$, $RS^-$, $OH^-$, and $Cl^-$

   Metals: $Sc^{3+}$, $Cu^+$, $W^{6+}$, $Mg^{2+}$, $V^{3+}$, $Fe^{3+}$, $Zr^{4+}$, $Co^{2+}$, $Ti^{4+}$, $Au^+$, $Al^{3+}$, and $Mn^{7+}$
7. Of $ReF_2$, $ReCl_5$, $MnF_6$, $Mn_2O_7$, and ReO, which are not likely to exist?
8. Of $WF_2$, $CrF_6$, $MoBr_6$, $WI_6$, $CrO_3$, $MoS_2$, $W_2S_3$, and MoH, which are not likely to exist?

### AnswerS

1. Metals in the +6 oxidation state are stabilized by oxide ($O^{2-}$) and fluoride ($F^-$). The M−F and M−O bonds are polar covalent due to extreme polarization of the anions by the highly charged metal. Ca, Sr, and Ba can be oxidized only to the dications ($M^{2+}$), which form ionic oxides and fluorides.
2.
3. Cyanide is a relatively soft base, and the early transition-metal cations are harder acids than the later transition metals.
4.
5. The formation of complexes between $NH_3$ and a divalent cation is largely due to electrostatic interactions between the negative end of the ammonia dipole moment and the positively charged cation. Thus the smallest divalent cations ($Ni^{2+}$, $Zn^{2+}$, and $Cu^{2+}$) will form the most stable complexes with ammonia.
6.

7. $Re^{2+}$ is a very soft cation, and $F^-$ and $O^{2-}$ are very hard bases, so ReO and $ReF_2$ are unlikely to exist. $MnF_6$ is also unlikely to exist: although fluoride should stabilize high oxidation states, in this case $Mn^{6+}$ is probably too small to accommodate six $F^-$ ions.

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# 22.5: Crystal Field Theory

**Learning Objectives**

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

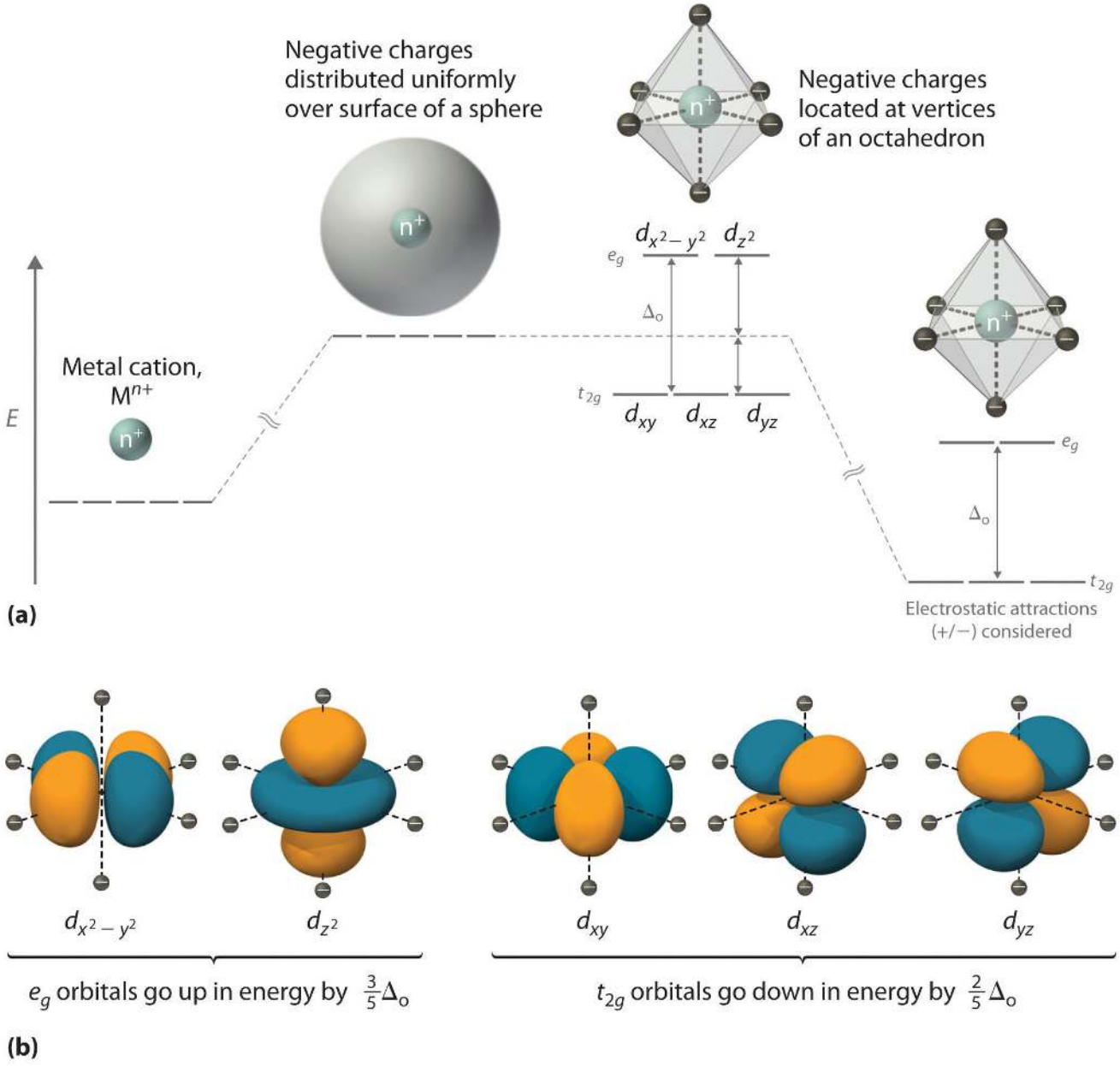
One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit (Figure 23.4 and Figure 23.5). In this section, we describe **crystal field theory (CFT)**, a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy.

## *d*-Orbital Splittings

CFT focuses on the interaction of the five $(n - 1)d$ orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model in Chapter 9, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the *d* orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall from Chapter 6 that the five *d* orbitals are initially degenerate (have the same energy). If we distribute six negative charges *uniformly* over the surface of a sphere, the *d* orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the *d* orbitals (part (a) in Figure 22.5.1. Placing the six negative charges at the vertices of an octahedron does not change the average energy of the *d* orbitals, but it does remove their degeneracy: the five *d* orbitals split into two groups whose energies depend on their orientations. As shown in part (b) in Figure 22.5.1, the dz2 and dx2−y2 orbitals point *directly* at the six negative charges located on the *x*, *y*, and *z* axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the $e_g$ orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three *d* orbitals ($d_{xy}$, $d_{xz}$, and $d_{yz}$, collectively called the $t_{2g}$ orbitals) are all oriented at a 45° angle to the coordinate axes, so they point *between* the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

Figure Figure 22.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five *d* Orbitals to Split into Two Sets with Different Energies




*(a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the dx2−y2 and dz2 orbitals increase in energy, while the, $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two $e_g$ orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three $t_{2g}$ orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.*

The difference in energy between the two sets of *d* orbitals is called the **crystal field splitting energy** ($\Delta_o$), where the subscript *o* stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: $\Delta_t$.) It is important to note that the splitting of the *d* orbitals in a crystal field does *not* change the total energy of the five *d* orbitals: the

two $e_g$ orbitals *increase* in energy by $0.6\Delta_o$, whereas the three $t_{2g}$ orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is $2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0$.

### Note the Pattern

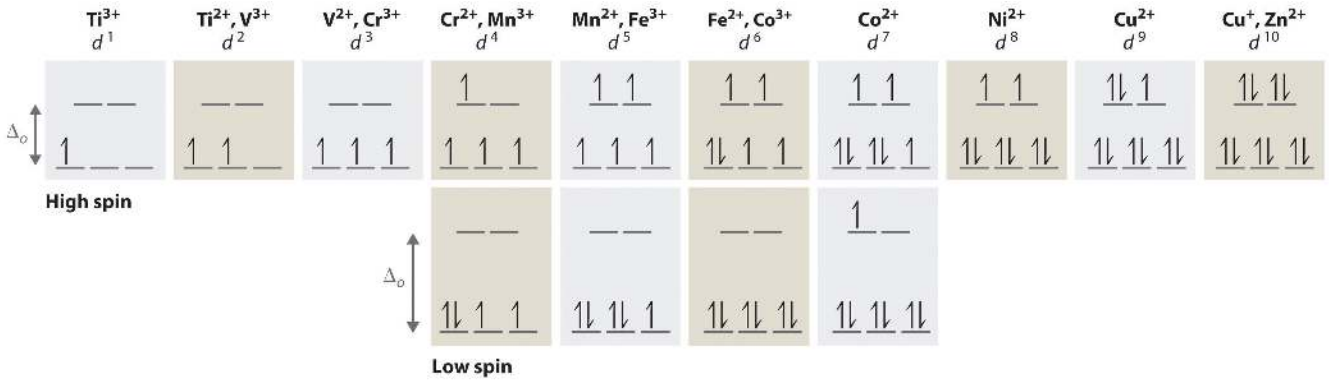
Crystal field splitting does not change the total energy of the *d* orbitals.

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the *d* orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the *d* orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five *d* orbitals without affecting their splitting (as shown at the far right in part (a) in Figure 22.5.1.

## Electronic Structures of Metal Complexes

We can use the *d*-orbital energy-level diagram in Figure 22.5.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the $Ti^{3+}$ ion, which contains a single *d* electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 22.5.2, for $d^1$–$d^3$ systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate $t_{2g}$ orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a $d^3$ electron configuration or, more succinctly, $Cr^{3+}$ is a $d^3$ ion.

Figure Figure 22.5.2 *The Possible Electron Configurations for Octahedral $d^n$ Transition-Metal Complexes (n = 1–10)*




*Two different configurations are possible for octahedral complexes of metals with $d^4$, $d^5$, $d^6$, and $d^7$ configurations; the magnitude of $\Delta_o$ determines which configuration is observed.*

When we reach the $d^4$ configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty $e_g$ orbitals or one of the singly occupied $t_{2g}$ orbitals. Recall from Chapter 6 that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the **spin-pairing energy (P)**. If $\Delta_o$ is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty $e_g$ orbitals. Because this arrangement results in four unpaired electrons, it is called a *high-spin configuration*, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a *high-spin complex*. Conversely, if $\Delta_o$ is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied $t_{2g}$ orbitals. Because this arrangement results in only two unpaired electrons, it is called a *low-spin configuration*, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a *low-spin complex*. Similarly, metal ions with the $d^5$, $d^6$, or $d^7$ electron configurations can be either high spin or low spin, depending on the magnitude of $\Delta_o$.

In contrast, only one arrangement of *d* electrons is possible for metal ions with $d^8$–$d^{10}$ electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is $d^8$ with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is $d^9$ with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is $d^{10}$ with no unpaired electrons.

### Note the Pattern

If $\Delta_o$ is less than the spin-pairing energy, a high-spin configuration results. Conversely, if $\Delta_o$ is greater, a low-spin configuration forms.

## Factors That Affect the Magnitude of $\Delta_o$

The magnitude of $\Delta_o$ dictates whether a complex with four, five, six, or seven *d* electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of $\Delta_o$ (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of $\Delta_o$ (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of $\Delta_o$ depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of $\Delta_o$ for some representative transition-metal complexes are given in Table 22.5.1".

Table 22.5.1 Crystal Field Splitting Energies for Some Octahedral ($\Delta_o$)* and Tetrahedral ($\Delta_t$) Transition-Metal Complexes

| Octahedral Complexes | $\Delta_o$ ($cm^{-1}$) | Octahedral Complexes | $\Delta_o$ ($cm^{-1}$) | Tetrahedral Complexes | $\Delta_t$ ($cm^{-1}$) |
|---|---|---|---|---|---|
| $[Ti(H_2O)_6]^{3+}$ | 20,300 | $[Fe(CN)_6]^{4-}$ | 32,800 | $VCl_4$ | 9010 |
| $[V(H_2O)_6]^{2+}$ | 12,600 | $[Fe(CN)_6]^{3-}$ | 35,000 | $[CoCl_4]^{2-}$ | 3300 |
| $[V(H_2O)_6]^{3+}$ | 18,900 | $[CoF_6]^{3-}$ | 13,000 | $[CoBr_4]^{2-}$ | 2900 |
| $[CrCl_6]^{3-}$ | 13,000 | $[Co(H_2O)_6]^{2+}$ | 9300 | $[CoI_4]^{2-}$ | 2700 |
| $[Cr(H_2O)_6]^{2+}$ | 13,900 | $[Co(H_2O)_6]^{3+}$ | 27,000 | | |
| $[Cr(H_2O)_6]^{3+}$ | 17,400 | $[Co(NH_3)_6]^{3+}$ | 22,900 | | |
| $[Cr(NH_3)_6]^{3+}$ | 21,500 | $[Co(CN)_6]^{3-}$ | 34,800 | | |
| $[Cr(CN)_6]^{3-}$ | 26,600 | $[Ni(H_2O)_6]^{2+}$ | 8500 | | |
| $Cr(CO)_6$ | 34,150 | $[Ni(NH_3)_6]^{2+}$ | 10,800 | | |
| $[MnCl_6]^{4-}$ | 7500 | $[RhCl_6]^{3-}$ | 20,400 | | |
| $[Mn(H_2O)_6]^{2+}$ | 8500 | $[Rh(H_2O)_6]^{3+}$ | 27,000 | | |
| $[MnCl_6]^{3-}$ | 20,000 | $[Rh(NH_3)_6]^{3+}$ | 34,000 | | |
| $[Mn(H_2O)_6]^{3+}$ | 21,000 | $[Rh(CN)_6]^{3-}$ | 45,500 | | |
| $[Fe(H_2O)_6]^{2+}$ | 10,400 | $[IrCl_6]^{3-}$ | 25,000 | | |
| $[Fe(H_2O)_6]^{3+}$ | 14,300 | $[Ir(NH_3)_6]^{3+}$ | 41,000 | | |

*Energies obtained by spectroscopic measurements are often given in units of *wave numbers* ($cm^{-1}$); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 $cm^{-1}$ = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, *Inorganic Chemistry*, 2nd ed. (New York: W. H. Freeman and Company, 1994).

## Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the *d* orbitals. Consequently, the magnitude of $\Delta_o$ increases as the charge on the metal ion increases. Typically, $\Delta_o$ for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, $\Delta_o$ = 11,800 $cm^{-1}$; for $[V(H_2O)_6]^{3+}$, $\Delta_o$ = 17,850 $cm^{-1}$.

## Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of $\Delta_o$ increases with increasing principal quantum number: $\Delta_o$ (3*d*) < $\Delta_o$ (4*d*) < $\Delta_o$ (5*d*). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

[Co(NH3)6]3+[Rh(NH3)6]3+[Ir(NH3)6]3+ΔoΔoΔo=22,900 cm−1=34,100 cm−1=40,000 cm−1

The increase in $\Delta_o$ with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger *d* orbital–ligand interactions.

## The Nature of the Ligands

Experimentally, it is found that the $\Delta_o$ observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of $\Delta_o$ decreases as the size of the donor atom increases. For example, $\Delta_o$ values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I^-$ because smaller, more localized charges, such as we see for $F^-$, interact more strongly with the *d* orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as $NH_3$, results in significantly larger $\Delta_o$ values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as $F^-$. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the **spectrochemical series**, shown here in order of decreasing $\Delta_o$:

CO≈CN−>strong-field ligandsNO2−>en>NH3>SCN−>H2O>oxalate2−intermediate-field ligands>OH−>F>acetate−>Cl−>Br−>I−weak-field ligands

The values of $\Delta_o$ listed in Table 22.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

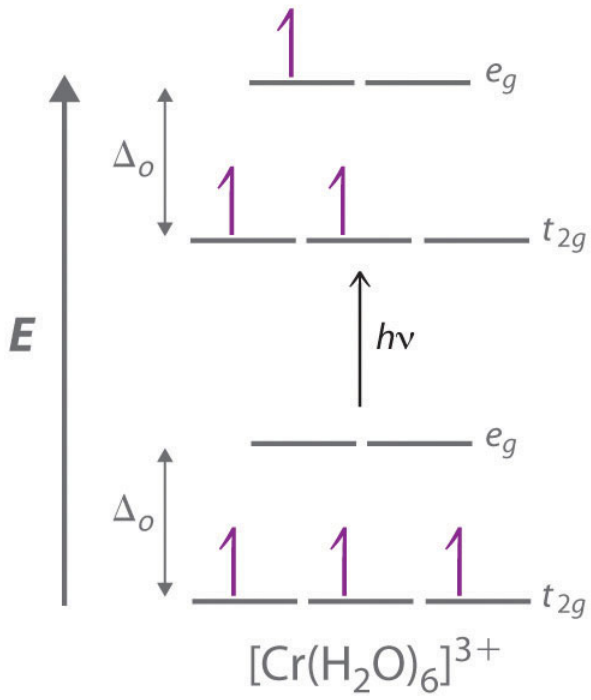
### Note the Pattern

The largest $\Delta_o$s are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.

## Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy *d* orbital to a higher-energy *d* orbital, which is called a *d–d transition* (Figure 22.5.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two *d* orbitals, which depends on the magnitude of $\Delta_o$.

Figure 22.5.3 *A d–d Transition*




*In a d–d transition, an electron in one of the $t_{2g}$ orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to $\Delta_o$, which causes the electron to move to an empty or singly occupied $e_g$ orbital.*

Recall from Chapter 6 that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel in End-of-Chapter Application Problem 6 in Chapter 6. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of $\Delta_o$, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large $\Delta_o$. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain $Cr^{3+}$ in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different ($Al_2O_3$ in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the *d* orbital–ligand interactions and makes $\Delta_o$ relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased *d* orbital–ligand interactions and a smaller $\Delta_o$. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



***Gem-quality crystals of ruby and emerald.*** *The colors of both minerals are due to the presence of small amounts of $Cr^{3+}$ impurities in octahedral sites in an otherwise colorless metal oxide lattice.*

## Crystal Field Stabilization Energies

Recall from Chapter 9 that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of *d* orbitals (the $t_{2g}$ orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single *d* electron in a $d^1$ complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the $t_{2g}$ orbitals. *Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$.* The additional stabilization of a metal complex by selective population of the lower-energy *d* orbitals is called its **crystal field stabilization energy (CFSE)**. The CFSE of a complex can be calculated by multiplying the number of electrons in $t_{2g}$ orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in $e_g$ orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 22.5.2 gives CFSE values for octahedral complexes with different *d* electron configurations. The CFSE is highest for low-spin $d^6$ complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the $d^3$ configuration.

Table 22.5.2 CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of $\Delta_o$)

| | High Spin | | CFSE ($\Delta_o$) | Low Spin | | CFSE ($\Delta_o$) |
|---|---|---|---|---|---|---|
| $d^0$ | | | 0 | | | |
| $d^1$ | ↑ | | 0.4 | | | |
| $d^2$ | ↑ ↑ | | 0.8 | | | |
| $d^3$ | ↑ ↑ ↑ | | 1.2 | | | |
| $d^4$ | ↑ ↑ ↑ | ↑ | 0.6 | ↑↓ ↑ ↑ | | 1.6 |
| $d^5$ | ↑ ↑ ↑ | ↑ ↑ | 0.0 | ↑↓ ↑↓ ↑ | | 2.0 |
| $d^6$ | ↑↓ ↑ ↑ | ↑ ↑ | 0.4 | ↑↓ ↑↓ ↑↓ | | 2.4 |
| $d^7$ | ↑↓ ↑↓ ↑ | ↑ ↑ | 0.8 | ↑↓ ↑↓ ↑↓ | ↑ | 1.8 |
| $d^8$ | ↑↓ ↑↓ ↑↓ | ↑ ↑ | 1.2 | | | |
| $d^9$ | ↑↓ ↑↓ ↑↓ | ↑↓ ↑ | 0.6 | | | |
| $d^{10}$ | ↑↓ ↑↓ ↑↓ | ↑↓ ↑↓ | 0.0 | | | |

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second,

CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

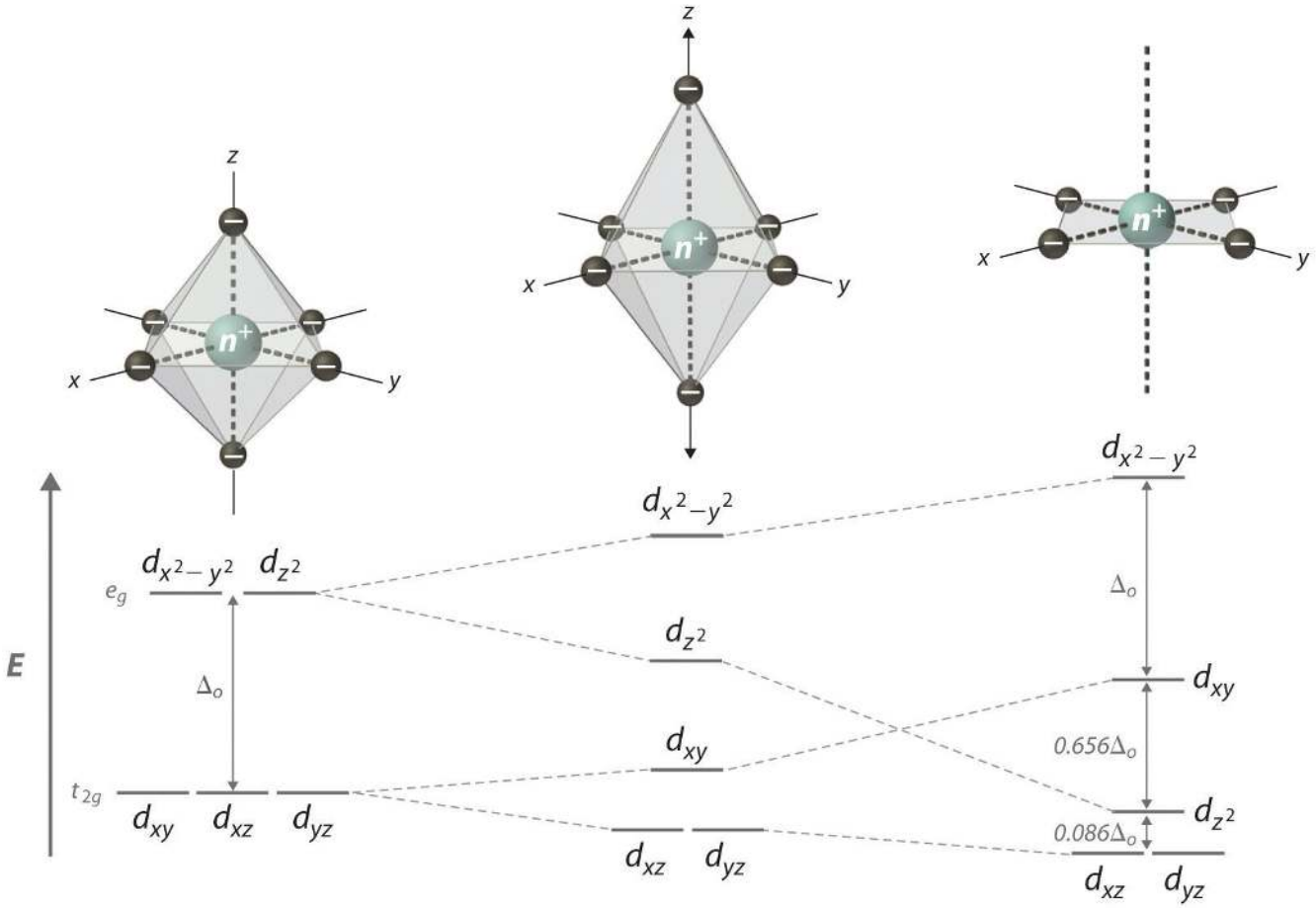
### Note the Pattern

Octahedral $d^3$ and $d^8$ complexes and low-spin $d^6$, $d^5$, $d^7$, and $d^4$ complexes exhibit large CFSEs.

## Tetragonal and Square Planar Complexes

If two *trans* ligands in an octahedral complex are either chemically different from the other four, as in the *trans*-$[Co(NH_3)_4Cl_2]^+$ ion, or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as $[Co(NH_3)_6]^{3+}$ and then slowly remove two *trans* $NH_3$ molecules by moving them away from the metal along the ±*z* axes, as shown in the top half of Figure 22.5.4 As the two axial Co–N distances increase simultaneously, the *d* orbitals that interact most strongly with the two axial ligands will *decrease* in energy due to a decrease in electrostatic repulsions between electrons in these orbitals and the negative ends of the ligand dipoles. The affected *d* orbitals are those with a component along the ±*z* axes—namely, dz2, $d_{xz}$, and $d_{yz}$. They will not be affected equally, however. Because the dz2 orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the energy of the other two, as shown in the bottom half of Figure 22.5.4. In addition, the positive charge on the metal will increase somewhat as the axial ligands are removed, causing the four remaining in-plane ligands to be more strongly attracted to the metal. This will increase their interactions with the other two *d* orbitals and increase their energy. Again, the two *d* orbitals will not be affected equally. Because the dx2−y2 orbital points directly at the four in-plane ligands, its energy will increase more rapidly than the energy of the $d_{xy}$ orbital, which points between the in-plane ligands. If we remove the two axial ligands to an infinite distance, we obtain a square planar complex. The energies of the dz2 and $d_{xy}$ orbitals actually cross as the axial ligands are removed, and the largest orbital spliting in a square planar complex is identical in magnitude to $\Delta_o$.

Figure 22.5.4 *d-Orbital Splittings for Tetragonal and Square Planar Complexes*

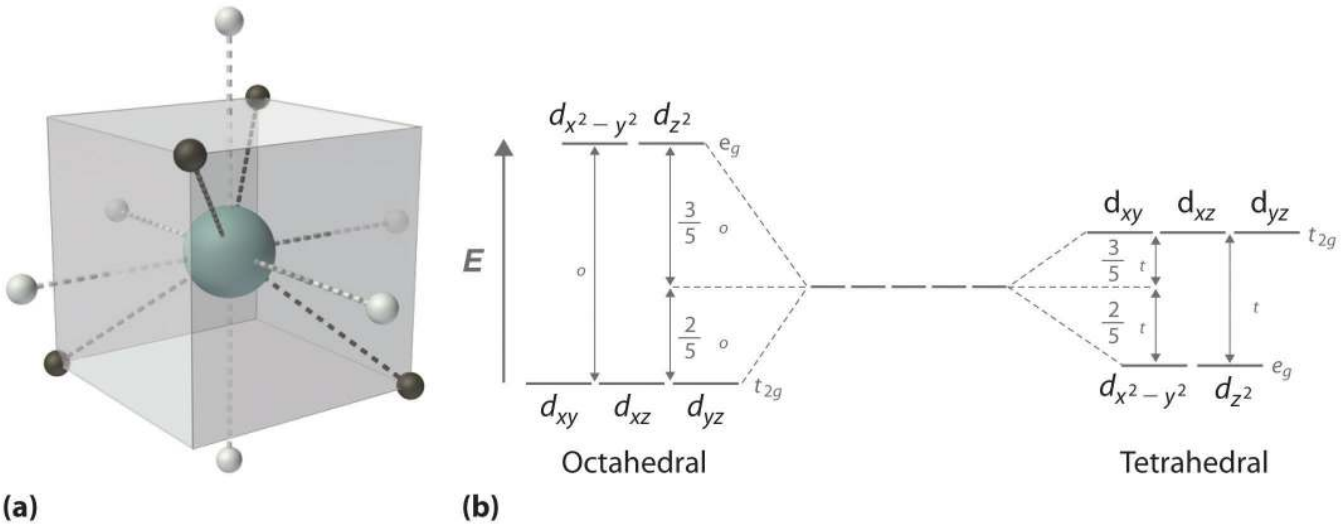



*Moving the two axial ligands away from the metal ion along the z axis initially gives an elongated octahedral complex (center) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes the dz2 $d_{xz}$ and $d_{yz}$ orbitals to decrease in energy and the dx2−y2 and $d_{xy}$ orbitals to increase in energy. As explained in the text, the change in energy is not the same for all five d orbitals. Removing the two axial ligands completely causes the energy of the dz2 orbital to decrease so much that the order of the dz2 and $d_{xy}$ orbitals is reversed.*

## Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (part (a) in Figure 22.5.5); consequently, none of the five *d* orbitals points directly at the ligands. Nonetheless, the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals interact more strongly with the ligands than do dx2−y2 and dz2 again resulting in a splitting of the five *d* orbitals into two sets. The splitting of the energies of the orbitals in a tetrahedral complex ($\Delta_t$) is much smaller than that for $\Delta_o$, however, for two reasons. First, the *d* orbitals interact less strongly with the ligands in a tetrahedral arrangement. Second, there are only four negative charges rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that, for complexes of the same metal ion with the same charge, the same ligands, and the same M–L distance, Δt=49Δo. The relationship between the splitting of the five *d* orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure 22.5.5.

Figure 22.5.5 *d-Orbital Splittings for a Tetrahedral Complex*




*(a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals (the $t_{2g}$ orbitals) interact more strongly with the ligands than do the dx2−y2 and dz2 orbitals (the $e_g$ orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex.*

### Note the Pattern

$\Delta_t < \Delta_o$ because of weaker *d*-orbital–ligand interactions and decreased electrostatic interactions.

Because $\Delta_o$ is so large for the second- and third-row transition metals, *all* four-coordinate complexes of these metals are square planar due to the much higher CFSE for square planar versus tetrahedral structures. The only exception is for $d^{10}$ metal ions such as $Cd^{2+}$, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral. The former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

### ✔ Example 22.5.1

1. $[CoF_6]^{3-}$
2. $[Rh(CO)_2Cl_2]^-$

**Given:** complexes

**Asked for:** structure, high spin versus low spin, and the number of unpaired electrons

**Solution**

**Strategy:**

**A** From the number of ligands, determine the coordination number of the compound.

**B** Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.

**C** Predict the relative magnitude of $\Delta_o$ and decide whether the compound is high spin or low spin.

**D** Place the appropriate number of electrons in the *d* orbitals and determine the number of unpaired electrons.

**Solution:**

1. **A** With six ligands, we expect this complex to be octahedral.

   **B** The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a $d^6$ electron configuration.

   **C** Because of the weak-field ligands, we expect a relatively small $\Delta_o$, making the compound high spin.

**D** In a high-spin octahedral $d^6$ complex, the first five electrons are placed individually in each of the *d* orbitals with their spins parallel, and the sixth electron is paired in one of the $t_{2g}$ orbitals, giving four unpaired electrons.

2. **A** This complex has four ligands, so it is either square planar or tetrahedral.

   **B C** Because rhodium is a second-row transition metal ion with a $d^8$ electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large $\Delta_o$, making it low spin. Because the strongest *d*-orbital interactions are along the *x* and *y* axes, the orbital energies increase in the order dz2$d_{yz}$, and $d_{xz}$ (these are degenerate); $d_{xy}$; and dx2−y2.

   **D** The eight electrons occupy the first four of these orbitals, leaving the dx2−y2. orbital empty. Thus there are no unpaired electrons.

**? Exercise 22.5.1**

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

1. $[Mn(H_2O)_6]^{2+}$
2. $[PtCl_4]^{2-}$

**Answer**

octahedral; high spin;

five square planar; low spin; no unpaired electrons

## Consequences of *d*-Orbital Splitting

The splitting of the *d* orbitals because of their interaction with the ligands in a complex has important consequences for the chemistry of transition-metal complexes; they can be divided into structural effects and thermodynamic effects. Although the two kinds of effects are interrelated, we will consider them separately.

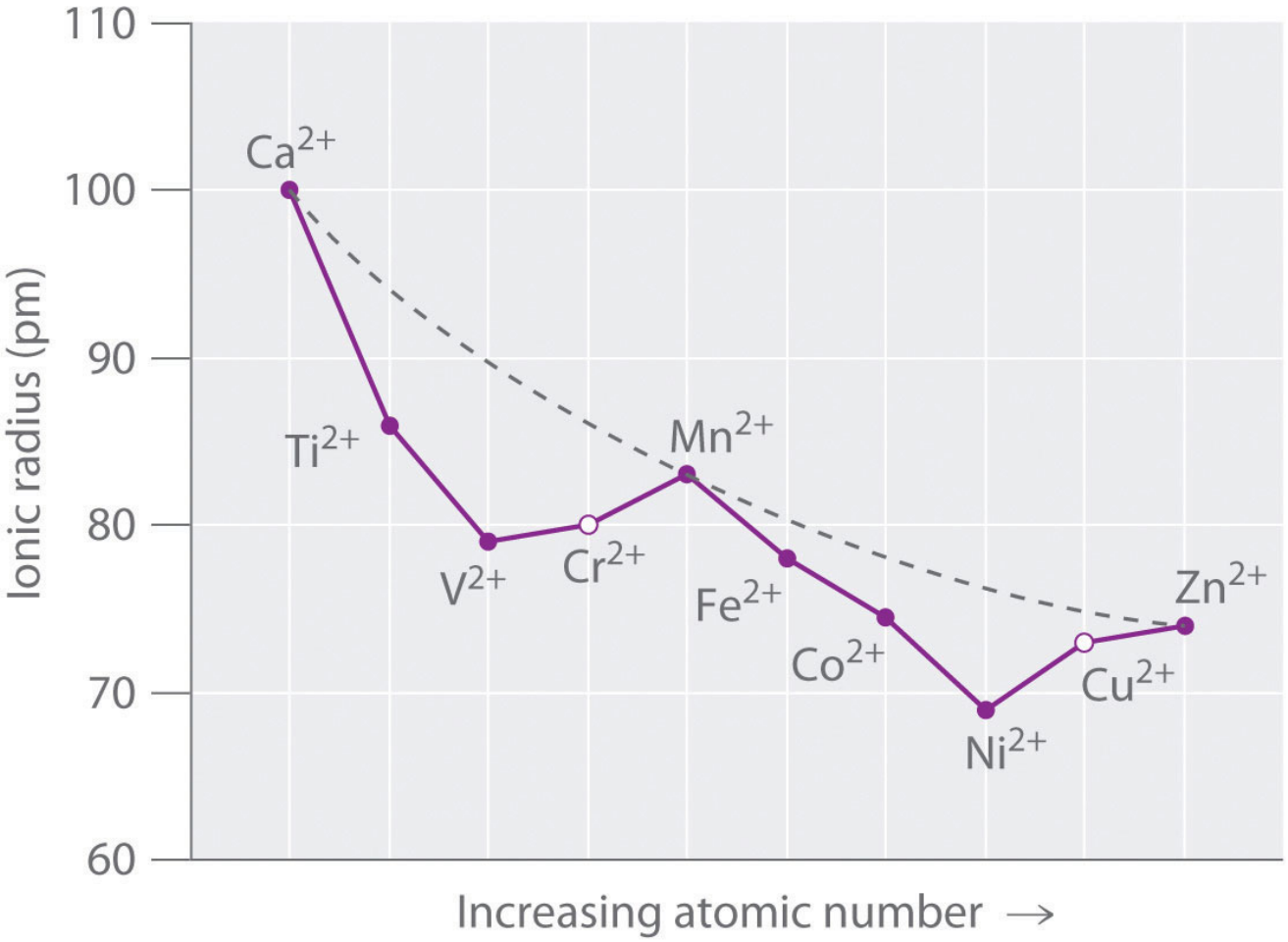
## Structural Effects

There are two major kinds of structural effects: effects on the ionic radius of metal ions with regular octahedral or tetrahedral geometries, and structural distortions that are observed for specific electron configurations.

### Ionic Radii

Figure 22.5.6 is a plot of the ionic radii of the divalent fourth-period metal ions versus atomic number. Only $Ca^{2+}$($d^0$), $Mn^{2+}$ (high-spin $d^5$), and $Zn^{2+}$ ($d^{10}$) fall on the smooth curve calculated based on the effective nuclear charge ($Z_{eff}$), which assumes that the distribution of *d* electrons is spherically symmetrical. *All the other divalent ions fall below this curve because they have asymmetrical distributions of d electrons*. (The points shown for $Cr^{2+}$ and $Cu^{2+}$ are only estimated values; as you will learn shortly, these two ions do not form any truly octahedral complexes.) To see why an asymmetrical distribution of *d* electrons makes a metal ion smaller than expected, consider the $Ti^{2+}$ ion, which has a $d^2$ configuration with both electrons in the $t_{2g}$ orbitals. Because the $t_{2g}$ orbitals are directed *between the ligands*, the two *d* electrons are unable to shield the ligands from the nuclear charge. Consequently, the ligands experience a higher effective nuclear charge than expected, the metal–ligand distance is unusually short, and the ionic radius is smaller than expected. If instead the two electrons were distributed uniformly over all five *d* orbitals, they would be much more effective at screening the ligands from the nuclear charge, making the metal–ligand distances longer and giving a larger ionic radius.

Figure 22.5.6 *The Effect of d-Orbital Splittings on the Radii of the Divalent Ions of the Fourth-Period Metals*




*Because these radii are based on the structures of octahedral complexes and $Cr^{2+}$ and $Cu^{2+}$ do not form truly octahedral complexes, the points for these ions are shown as open circles. The dashed line represents the behavior predicted based on the effects of screening and variation in effective nuclear charge ($Z_{eff}$), assuming a spherical distribution of the 3d electrons.*

A similar effect is observed for the $V^{2+}$ ion, which has a $d^3$ configuration. Because the three electrons in the $t_{2g}$ orbitals provide essentially no shielding of the ligands from the metal, the ligands experience the full increase of +1 in nuclear charge that occurs in going from $Ti^{2+}$ to $V^{2+}$. Consequently, the observed ionic radius of the $V^{2+}$ ion is significantly smaller than that of the $Ti^{2+}$ ion.

Skipping the $Cr^{2+}$ ion for the moment, we next consider the $d^5$ $Mn^{2+}$ ion. Because the nuclear charge increases by +2 from $V^{2+}$ to $Mn^{2+}$, we might expect $Mn^{2+}$ to be smaller than $V^{2+}$. The two electrons that are also added from $V^{2+}$ to $Mn^{2+}$ occupy the $e_g$ orbitals, however, which point directly at the six ligands. Because these electrons are localized directly between the metal ion and the ligands, they are effective at screening the ligands from the increased nuclear charge. As a result, the ionic radius actually *increases* significantly as we go from $V^{2+}$ to $Mn^{2+}$, despite the higher nuclear charge of the latter.

Exactly the same effects are seen in the second half of the first-row transition metals. In the $Fe^{2+}$, $Co^{2+}$, and $Ni^{2+}$ ions, the extra electrons are added successively to the $t_{2g}$ orbitals, resulting in poor shielding of the ligands from the nuclear charge and abnormally small ionic radii. Skipping over $Cu^{2+}$, we again see that adding the last two electrons causes a significant increase in the ionic radius of $Zn^{2+}$, despite its higher nuclear charge.

## The Jahn–Teller Effect

Because simple octahedral complexes are not known for the $Cr^{2+}$ and $Cu^{2+}$ ions, only estimated values for their radii are shown in Figure 22.5.6. We see in Figure 22.5.7 that both the $Cr^{2+}$ and $Cu^{2+}$ ions have electron configurations with an odd number of electrons in the $e_g$ orbitals. Because the single electron (in the case of $Cr^{2+}$) or the third electron (in the case of $Cu^{2+}$) can occupy

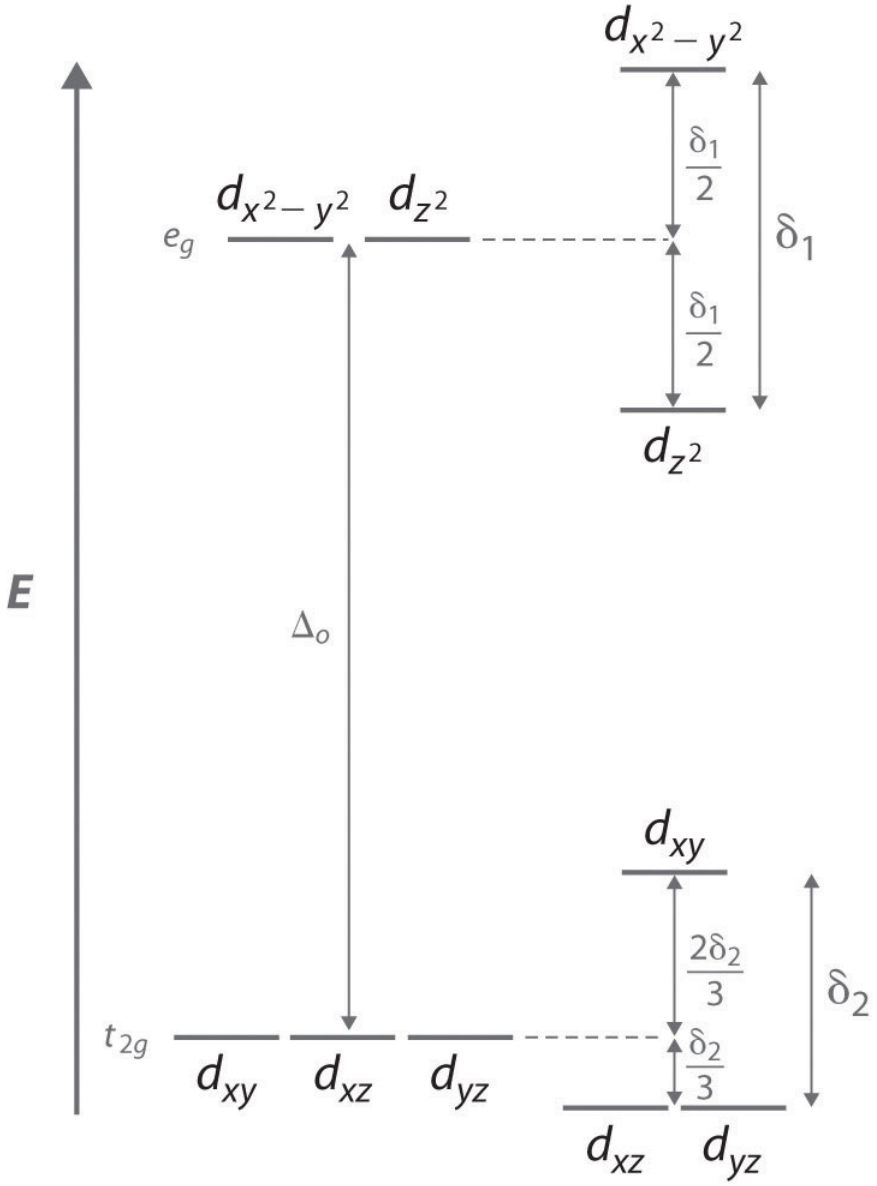
either one of two degenerate $e_g$ orbitals, they have what is called a *degenerate ground state*. The **Jahn–Teller theorem** states that such non-linear systems are not stable; they will undergo a distortion that makes the complex less symmetrical and splits the degenerate states, which decreases the energy of the system. The distortion and resulting decrease in energy are collectively referred to as the *Jahn–Teller effect*. Neither the nature of the distortion nor its magnitude is specified, and in fact, they are difficult to predict. In principle, Jahn–Teller distortions are possible for many transition-metal ions; in practice, however, they are observed only for systems with an odd number of electrons in the $e_g$ orbitals, such as the $Cr^{2+}$ and $Cu^{2+}$ ions.

To see how a geometrical distortion can decrease the energy of such a system, consider an octahedral $Cu^{2+}$ complex, the $[Cu(H_2O)_6]^{2+}$ ion, which has been elongated along the *z* axis. As indicated in Figure 22.5.7, this kind of distortion splits both the $e_g$ and $t_{2g}$ sets of orbitals. Because the axial ligands interact most strongly with the dz2 orbital, the splitting of the $e_g$ set ($\delta_1$) is significantly larger than the splitting of the $t_{2g}$ set ($\delta_2$), but both $\delta_1$ and $\delta_2$ are much, much smaller than the $\Delta_o$. This splitting does not change the center of gravity of the energy within each set, so a Jahn–Teller distortion results in no net change in energy for a filled or half-filled set of orbitals. If, however, the $e_g$ set contains one (as in the $d^4$ ions, $Cr^{2+}$ and $Mn^{3+}$) or three (as in the $d^9$ ion, $Cu^{2+}$) electrons, the distortion decreases the energy of the system. For $Cu^{2+}$, for example, the change in energy after distortion is $2(-\delta_1/2) + 1(\delta_1/2) = -\delta_1/2$. For $Cu^{2+}$ complexes, the observed distortion is *always* an elongation along the *z* axis by as much as 50 pm; in fact, many $Cu^{2+}$ complexes are so distorted that they are effectively square planar. In contrast, the distortion observed for most $Cr^{2+}$ complexes is a *compression* along the *z* axis. In both cases, however, the net effect is the same: the distorted system is more stable than the undistorted system.

### Note the Pattern

Jahn–Teller distortions are most important for $d^9$ and high-spin $d^4$ complexes; the distorted system is more stable than the undistorted one.

Figure 22.5.7*The Jahn–Teller Effect*




*Increasing the axial metal–ligand distances in an octahedral $d^9$ complex is an example of a Jahn–Teller distortion, which causes the degenerate pair of $e_g$ orbitals to split in energy by an amount $\delta_1$; $\delta_1$ and $\delta_2$ are much smaller than $\Delta_o$. As a result, the distorted system is more stable (lower in energy) than the undistorted complex by $\delta_1/2$.*

## Thermodynamic Effects

As we previously noted, CFSEs can be as large as several hundred kilojoules per mole, which is the same magnitude as the strength of many chemical bonds or the energy change in most chemical reactions. Consequently, CFSEs are important factors in determining the magnitude of hydration energies, lattice energies, and other thermodynamic properties of the transition metals.

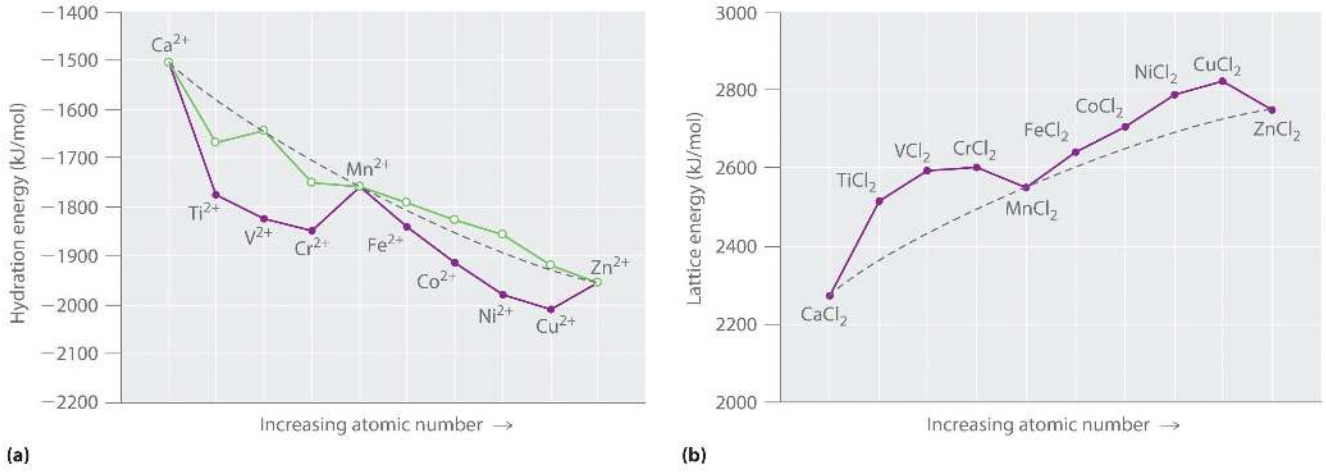
## Hydration Energies

The hydration energy of a metal ion is defined as the change in enthalpy for the following reaction:

\( $M^{2+}(g) + H_2O(l) \rightarrow M^{2+}(aq)$ \)

Although hydration energies cannot be measured directly, they can be calculated from experimentally measured quantities using thermochemical cycles. As shown in part (a) in Figure 22.5.8, a plot of the hydration energies of the fourth-period metal dications versus atomic number gives a curve with two valleys. Note the relationship between the plot in part (a) in Figure 22.5.8" and the plot of ionic radii in Figure 22.5.6: the overall shapes are essentially identical, and only the three cations with spherically symmetrical distributions of *d* electrons ($Ca^{2+}$, $Mn^{2+}$, and $Zn^{2+}$) lie on the dashed lines. In part (a) in Figure 22.5.8 the dashed line corresponds to hydration energies calculated based solely on electrostatic interactions. Subtracting the CFSE values for the $[M(H_2O)_6]^{2+}$ ions from the experimentally determined hydration energies gives the points shown as open circles, which lie very near the calculated curve. Thus CFSEs are primarily responsible for the differences between the measured and calculated values of hydration energies.

Figure 22.5.8 *Thermochemical Effects of d-Orbital Splittings*




*(a) A plot of the hydration energies of the divalent fourth-period metal ions versus atomic number (solid circles) shows large deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed line). Correcting for CFSE gives the points shown as open circles, which, except for $Ti^{2+}$ and $Cr^{2+}$, are close to the calculated values. The apparent deviations for these ions are caused by the fact that solutions of the $Ti^{2+}$ ion in water are not stable, and $Cr^{2+}$ does not form truly octahedral complexes. (b) A plot of the lattice energies for the fourth-period metal dichlorides versus atomic number shows similar deviations from the smooth curve calculated, assuming a spherical distribution of d electrons (dashed lines), again illustrating the importance of CFSEs.*

## Lattice Energies

Values of the lattice energies for the fourth-period metal dichlorides are plotted versus atomic number in part (b) in Figure 22.5.8. Recall that the lattice energy is defined as the negative of the enthalpy change for the following reaction. Like hydration energies, lattice energies are determined indirectly by using a thermochemical cycle:

\( M^{2+}(g) + 2Cl^{-}(g) \rightarrow MCl_2(s) \)

The shape of the lattice-energy curve is essentially the mirror image of the hydration-energy curve in part (a) in Figure 23.19, with only $Ca^{2+}$, $Mn^{2+}$, and $Zn^{2+}$ lying on the smooth curve. It is not surprising that the explanation for the deviations from the curve is exactly the same as for the hydration energy data: all the transition-metal dichlorides, except $MnCl_2$ and $ZnCl_2$, are more stable than expected due to CFSE.

### Summary

**Crystal field theory (CFT)** is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the *d* orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the **crystal field splitting energy ($\Delta_o$)**, whose magnitude depends on the charge on the metal ion, the position of the metal in

the periodic table, and the nature of the ligands. The **spin-pairing energy (P)** is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the $\Delta_o$ is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the $\Delta_o$ is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the *d* orbitals of the metal ions and give a large $\Delta_o$, whereas weak-field ligands interact more weakly and give a smaller $\Delta_o$. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT. Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the *d* orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy $\Delta_t$. The **crystal field stabilization energy (CFSE)** is the additional stabilization of a complex due to placing electrons in the lower-energy set of *d* orbitals. CFSE explains the unusual curves seen in plots of ionic radii, hydration energies, and lattice energies versus atomic number. The **Jahn–Teller theorem** states that a non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion to remove the degeneracy and lower the overall energy of the system.

## KEY TAKEAWAY

- Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity.

## CONCEPTUAL PROBLEMS

1. Describe crystal field theory in terms of its
    1. assumptions regarding metal–ligand interactions.
    2. weaknesses and strengths compared with valence bond theory.
2. In CFT, what causes degenerate sets of *d* orbitals to split into different energy levels? What is this splitting called? On what does the magnitude of the splitting depend?
3. Will the value of $\Delta_o$ increase or decrease if $I^-$ ligands are replaced by $NO_2^-$ ligands? Why?
4. For an octahedral complex of a metal ion with a $d^6$ configuration, what factors favor a high-spin configuration versus a low-spin configuration?
5. How can CFT explain the color of a transition-metal complex?

## STRUCTURE AND REACTIVITY

1. Do strong-field ligands favor a tetrahedral or a square planar structure? Why?
2. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.
    1. $[TiCl_6]^{3-}$
    2. $[CoCl_4]^{2-}$
3. For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.
    1. $[Cu(NH_3)_4]^{2+}$
    2. $[Ni(CN)_4]^{2-}$
4. The ionic radii of $V^{2+}$, $Fe^{2+}$, and $Zn^{2+}$ are all roughly the same (approximately 76 pm). Given their positions in the periodic table, explain why their ionic radii are so similar.

### Answer

1. 
2. 
3. 1. $d^9$, square planar, neither high nor low spin, single unpaired electron
    2. $d^8$, square planar, low spin, no unpaired electrons

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# 22.6: Transition Metals in Biology

**Learning Objectives**

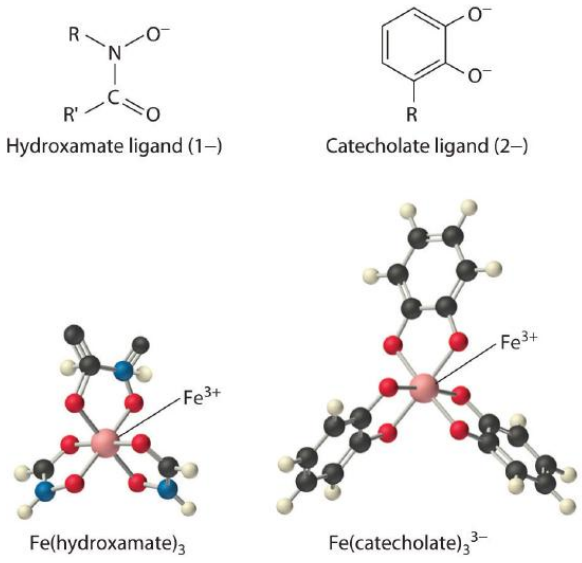
- To become familiar with some of the roles of transition-metal complexes in biological systems.

In this section, we describe several systems that illustrate the roles transition metals play in biological systems. Our goal is for you to understand why the chemical properties of these elements make them essential for life. We begin with a discussion of the strategies organisms use to extract transition metals from their environment. The section continues with a brief discussion of the use of transition metals in reactions that involve the transfer of electrons, reactions of small molecules such as $O_2$, Lewis-acid catalysis, and the generation of reactive organic radicals.

## Uptake and Storage of Transition Metals

There are three possible dietary levels for any essential element: deficient, optimal, and toxic, in order of increasing concentration in the diet. If the concentration of an essential element in the diet is too low, an organism must be able to extract the element from the environment and concentrate it. If the concentration of an essential element in the diet is too high, an organism must be able to limit its intake to avoid toxic effects. Moreover, organisms must be able to switch off the uptake process rapidly if dietary levels rise suddenly, and they must be able to store essential elements for future use.

Three distinct steps are involved in transition metal uptake. First, the metal must be "mobilized" from the environment and brought into contact with a cell in a form that can be absorbed. Second, the metal must be transported across the cell membrane into the cell. Third, the element must be transported to its point of utilization within a cell or to other cells within the organism. In our discussion, we focus on the uptake, transport, and storage of iron, which illustrates the most important points. Because iron deficiency (anemia) is the most widespread nutritional deficiency known in humans, the uptake of iron is especially well understood.




*Iron complexes in biological systems. Iron(III) forms very stable octahedral complexes with hydroxamate and catecholate ligands.*

The solubility of metal ions such as $Fe^{3+}$, which form highly insoluble hydroxides, depends on the pH and the presence of complexing agents. In an oxygen-containing atmosphere, iron exists as Fe(III) because of the positive reduction potential of $Fe^{3+}$ ($Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E° = +0.77$ V). Because ferric hydroxide [$Fe(OH)_3$] is highly insoluble ($K_{sp} \approx 1 \times 10^{-39}$), the equilibrium concentration of $Fe^{3+}(aq)$ at pH 7.0 is very low, about $10^{-18}$ M. You would have to drink $2 \times 10^{13}$ L of iron-saturated water per day (roughly 5 $mi^3$) to consume the recommended daily intake of Fe for humans, which is about 1 mg/day. Animals such as humans can overcome this problem by consuming concentrated sources of iron, such as red meat, but microorganisms cannot.

Consequently, most microorganisms synthesize and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Siderophores are generally cyclic compounds that use bidentate ligands, such as the hydroxamate and catecholate groups shown here, to bind $Fe^{3+}$ in an octahedral arrangement. Typical siderophores are ferrichrome, a cyclic peptide produced by fungi, and enterobactin, a cyclic ester produced by bacteria (Figure 22.6.1). Attaching the three iron ligands to a cyclic framework greatly increases the stability of the resulting $Fe^{3+}$ complex due to the chelate effect described in Section 23.4. The formation constants for the $Fe^{3+}$ complexes of ferrichrome and enterobactin are about $10^{32}$ and $10^{40}$, respectively, which are high enough to allow them to dissolve almost any Fe(III) compound.

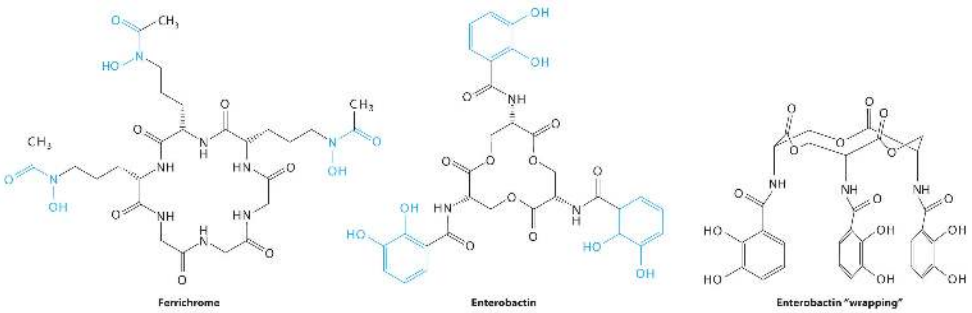



Figure 22.6.1: Siderophores. Ferrichrome (a) and enterobactin (b) are siderophores that use hydroxamate and catecholate ligands, respectively, to bind $Fe^{3+}$. The "wrapped" drawing of enterobactin (c) shows how the cyclic ester framework places the three catecholate ligands in the correct orientation to bind to a single $Fe^{3+}$ ion, which is an application of the chelate effect. The actual structure of ferrichrome is similar to that of enterobactin, with the three hydroxamate ligands adjacent to one another for optimal binding of $Fe^{3+}$. Note: For clarity, most or all hydrogen atoms have been omitted in this and the following structures.

Siderophores increase the $[Fe^{3+}]$ in solution, providing the bacterium that synthesized them (as well as any competitors) with a supply of iron. In addition, siderophores neutralize the positive charge on the metal ion and provide a hydrophobic "wrapping" that enables the $Fe^{3+}$–siderophore complex to be recognized by a specific protein that transports it into the interior of a cell. Once it is inside a cell, the iron is reduced to $Fe^{2+}$, which has a much lower affinity for the siderophore and spontaneously dissociates.

In contrast, multicellular organisms can increase the concentration of iron in their diet by lowering the pH in the gastrointestinal tract. At pH 1.0 (the approximate pH of the stomach), most Fe(III) salts dissolve to form $Fe^{3+}(aq)$, which is absorbed by specific proteins in the intestinal wall. A protein called transferrin forms a complex with iron(III), allowing it to be transported to other cells. Proteins that bind tightly to Fe(III) can also be used as antibacterial agents because iron is absolutely essential for bacterial growth. For example, milk, tears, and egg white all contain proteins similar to transferrin, and their high affinity for $Fe^{3+}$ allows them to sequester iron, thereby preventing bacteria from growing in these nutrient-rich media.

Iron is released from transferrin by reduction to $Fe^{2+}$, and then it is either used immediately (e.g., for the synthesis of hemoglobin) or stored in a very large protein called ferritin for future use (Figure 22.6.2). Ferritin uses oxygen to oxidize $Fe^{2+}$ to $Fe^{3+}$, which at neutral pH precipitates in the central cavity of the protein as a polymeric mixture of $Fe(OH)_3$ and $FePO_4$. Because a fully loaded ferritin molecule can contain as many as 4500 Fe atoms, which corresponds to about 25% Fe by mass, ferritin is an effective way to store iron in a highly concentrated form. When iron is needed by a cell, the $Fe^{3+}$ is reduced to the much more soluble $Fe^{2+}$ by a reductant such as ascorbic acid (vitamin C). The structure of ferritin contains channels at the junctions of the subunits, which provide pathways for iron to enter and leave the interior of a molecule.

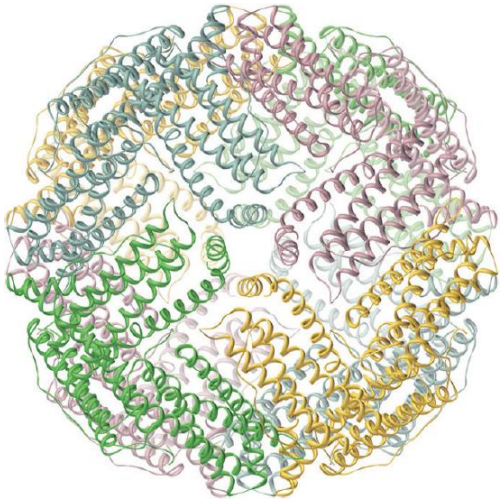


Figure 22.6.2: Ferritin, an Iron Storage Protein. A schematic drawing of the structure of iron-loaded ferritin, showing the almost spherical protein shell inside which the iron hydroxide/phosphate core is formed.

## Metalloproteins and Metalloenzymes

A protein that contains one or more metal ions tightly bound to amino acid side chains is called a metalloprotein; some of the most common ligands provided by amino acids are shown here. A metalloprotein that catalyzes a chemical reaction is a metalloenzyme. Thus all metalloenzymes are metalloproteins, but the converse is not true. Recent estimates suggest that more than 40% of all known enzymes require at least one metal ion for activity, including almost all the enzymes responsible for the synthesis, duplication, and repair of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).

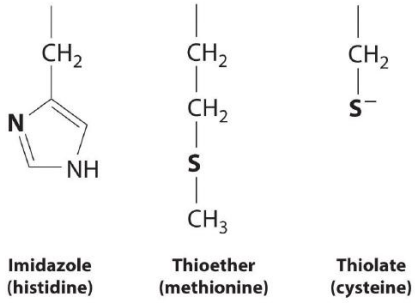



Figure 22.6.2b: Ligands used in biological systems. These metal ligands are commonly found in metalloproteins.

## Electron-Transfer Proteins

Proteins whose function is to transfer electrons from one place to another are called electron-transfer proteins. Because they do not catalyze a chemical reaction, electron-transfer proteins are not enzymes; they are biochemical reductants or oxidants consumed in an enzymatic reaction. The general reaction for an electron-transfer protein is as follows:

$$M^{n+} + e^- \rightleftharpoons M^{(n-1)+} \tag{22.6.1}$$

Because many transition metals can exist in more than one oxidation state, electron-transfer proteins usually contain one or more metal ions that can undergo a redox reaction. Incorporating a metal ion into a protein has three important biological consequences:

1. The protein environment can adjust the redox potential ($E^{0\prime}$), of the metal ion over a rather large potential range, whereas the redox potential of the simple hydrated metal ion [$M_n^+$(aq)], is essentially fixed.
2. The protein can adjust the structure of the metal complex to ensure that electron transfer is rapid.
3. The protein environment provides specificity, ensuring that the electron is transferred to only the desired site.

Three important classes of metalloproteins transfer electrons: blue copper proteins, cytochromes, and iron–sulfur proteins, which generally transfer electrons at high (> 0.20 V), intermediate (±0 V), and low (−0.20 to −0.50 V) potentials, respectively (Table 23.12). Although these electron-transfer proteins contain different metals with different structures, they are all designed to ensure

rapid electron transfer to and from the metal. Thus when the protein collides with its physiological oxidant or reductant, electron transfer can occur before the two proteins diffuse apart. For electron transfer to be rapid, the metal sites in the oxidized and reduced forms of the protein must have similar structures.

Table 22.6.1: Some Properties of the Most Common Electron-Transfer Proteins

| Protein | Metal Center | M/e− Transferred | Reduction Potential (V) |
|---|---|---|---|
| iron–sulfur proteins* | $[Fe(SR)_4]^{2-}$ | 1 Fe | −0.1 to +0.1 |
| | $[(RS)_2FeS_2Fe(SR)_2]^{2-}$ | 2 Fe | −0.2 to −0.4 |
| | $[Fe_3S_4(SR)_3]^{3-}$ | 3 Fe | −0.1 to −0.2 |
| | $[Fe_4S_4(SR)_4]^{2-}$ | 4 Fe | −0.3 to −0.5 |
| cytochromes | Fe-heme (low spin) | 1 Fe | ~0 |
| blue copper proteins† | $[Cu(Im)_2(SR)(SR_2)]^-$ | 1 Cu | ≥ +0.20 |

* A sulfur bound to an organic group is represented as SR.

† See Figure 22.6.2*b*: for the structure of imidazole (Im).

## Blue Copper Proteins

Blue copper proteins were first isolated from bacteria in the 1950s and from plant tissues in the early 1960s. The intense blue color of these proteins is due to a strong absorption band at a wavelength of about 600 nm. Although simple $Cu^{2+}$ complexes, such as $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, are also blue due to an absorption band at 600 nm, the intensity of the absorption band is about 100 times less than that of a blue copper protein. Moreover, the reduction potential for the $Cu^{2+}/Cu^+$ couple in a blue copper protein is usually +0.3 to +0.5 V, considerably more positive than that of the aqueous $Cu^{2+}/Cu^+$ couple (+0.15 V).

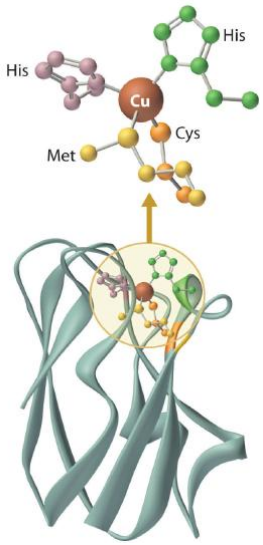



Figure 22.6.3: A Blue Copper Protein. In both the oxidized and reduced forms of a blue copper protein, the copper is coordinated by four ligands (two histidine imidazole nitrogen atoms, a cysteine thiolate sulfur, and a thioether sulfur of a methionine) in a roughly tetrahedral arrangement.

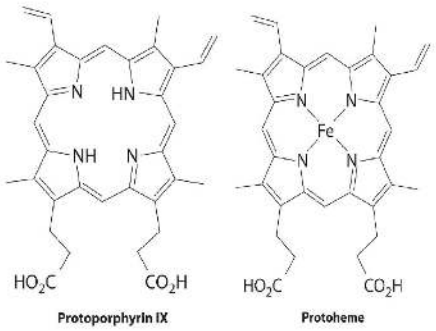
The copper center in blue copper proteins has a distorted tetrahedral structure, in which the copper is bound to four amino acid side chains (Figure 22.6.3). Although the most common structures for four-coordinate $Cu^{2+}$ and $Cu^+$ complexes are square planar and tetrahedral, respectively, the structures of the oxidized ($Cu^{2+}$) and reduced ($Cu^+$) forms of the protein are essentially identical. Thus the protein forces the $Cu^{2+}$ ion to adopt a higher-energy structure that is more suitable for $Cu^+$, which makes the $Cu^{2+}$ form easier to reduce and raises its reduction potential.

Moreover, by forcing the oxidized and reduced forms of the metal complex to have essentially the same structure, the protein ensures that electron transfer to and from the copper site is rapid because only minimal structural reorganization of the metal center is required. Kinetics studies on simple metal complexes have shown that electron-transfer reactions tend to be slow when the structures of the oxidized and reduced forms of a metal complex are very different, and fast when they are similar. You will see that other metal centers used for biological electron-transfer reactions are also set up for minimal structural reorganization after electron transfer, which ensures the rapid transfer of electrons.

## Cytochromes

The cytochromes (from the Greek cytos, meaning “cell”, and chroma, meaning “color”) were first identified in the 1920s by spectroscopic studies of cell extracts. Based on the wavelength of the maximum absorption in the visible spectrum, they were classified as cytochromes a (with the longest wavelength), cytochromes b (intermediate wavelength), and cytochromes c (shortest wavelength). It quickly became apparent that there was a correlation between their spectroscopic properties and other physical properties. For examples, cytochromes c are generally small, soluble proteins with a reduction potential of about +0.25 V, whereas cytochromes b are larger, less-soluble proteins with reduction potentials of about 0 V.

All cytochromes contain iron, and the iron atom in all cytochromes is coordinated by a planar array of four nitrogen atoms provided by a cyclic tetradentate ligand called a porphyrin. The iron–porphyrin unit is called a heme group. The structures of a typical porphyrin (protoporphyrin IX) and its iron complex (protoheme) are shown here. In addition to the four nitrogen atoms of the porphyrin, the iron in a cytochrome is usually bonded to two additional ligands provided by the protein, as shown in Figure 22.6.4.




A cytochrome. Shown here is protoporphyrin IX and its iron complex, protoheme.

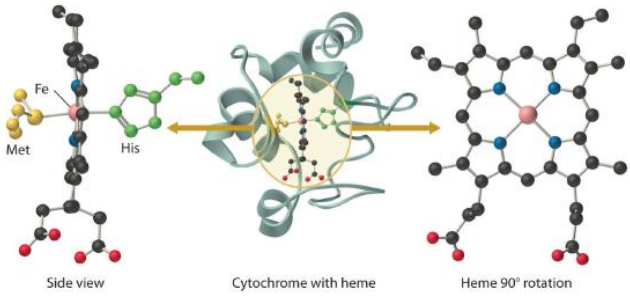



Figure 22.6.4: A Cytochrome c. In a cytochrome c, the heme iron is coordinated to the nitrogen atom of a histidine imidazole and the sulfur atom of a methionine thioether, in addition to the four nitrogen atoms provided by the porphyrin.

In contrast to the blue copper proteins, two electron configurations are possible for both the oxidized and reduced forms of a cytochrome, and this has significant structural consequences. Thus $Fe^{2+}$ is $d^6$ and can be either high spin (with four unpaired electrons) or low spin (with no unpaired electrons). Similarly, $Fe^{3+}$ is $d^5$ and can also be high spin (with five unpaired electrons) or low spin (with one unpaired electron). In low-spin heme complexes, both the $Fe^{2+}$ and the $Fe^{3+}$ ions are small enough to fit into the “hole” in the center of the porphyrin; hence the iron atom lies almost exactly in the plane of the four porphyrin nitrogen atoms in both cases. Because cytochromes b and c are low spin in both their oxidized and reduced forms, the structures of the oxidized and reduced cytochromes are essentially identical. Hence minimal structural changes occur after oxidation or reduction, which makes electron transfer to or from the heme very rapid.

> *Electron transfer reactions occur most rapidly when minimal structural changes occur during oxidation or reduction.*

### Iron–Sulfur Proteins

Although all known bacteria, plants, and animals use iron–sulfur proteins to transfer electrons, the existence of these proteins was not recognized until the late 1950s. Iron–sulfur proteins transfer electrons over a wide range of reduction potentials, and their iron content can range from 1 to more than 12 Fe atoms per protein molecule. In addition, most iron–sulfur proteins contain stoichiometric amounts of sulfide ($S^{2-}$).

These properties are due to the presence of four different kinds of iron–sulfur units, which contain one, two, three, or four iron atoms per Fe–S complex (Figure 22.6.5). In all cases, the $Fe^{2+}$ and $Fe^{3+}$ ions are coordinated to four sulfur ligands in a tetrahedral environment. Due to tetrahedral coordination by weak-field sulfur ligands, the iron is high spin in both the $Fe^{3+}$ and $Fe^{2+}$ oxidation states, which results in similar structures for the oxidized and reduced forms of the Fe–S complexes. Consequently, only small structural changes occur after oxidation or reduction of the Fe–S center, which results in rapid electron transfer.

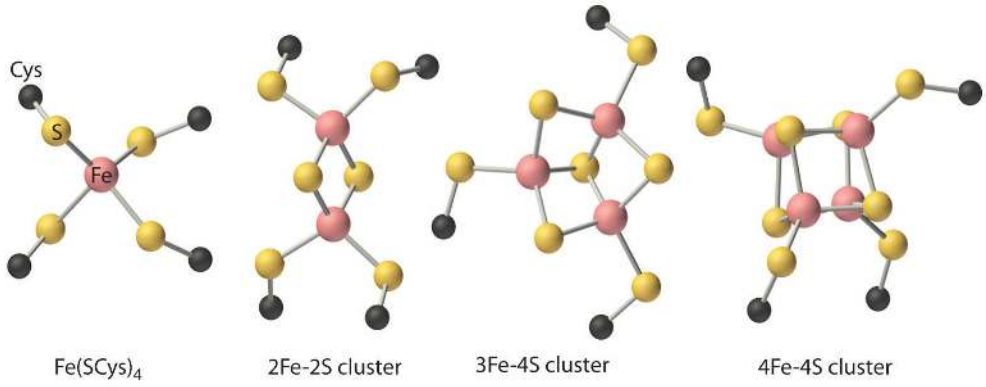



Figure 22.6.5: Fe–S Centers in Proteins: Four kinds of iron–sulfur centers, containing one, two, three, and four iron atoms, respectively, are known in electron-transfer proteins. Although they differ in the number of sulfur atoms provided by cysteine thiolates versus sulfide, in all cases the iron is coordinated to four sulfur ligands in a roughly tetrahedral environment.

## Reactions of Small Molecules

Although small molecules, such as $O_2$, $N_2$, and $H_2$, do not react with organic compounds under ambient conditions, they do react with many transition-metal complexes. Consequently, virtually all organisms use metalloproteins to bind, transport, and catalyze the reactions of these molecules. Probably the best-known example is hemoglobin, which is used to transport $O_2$ in many multicellular organisms.

> *Under ambient conditions, small molecules, such as $O_2$, $N_2$, and $H_2$, react with transition-metal complexes but not with organic compounds.*

### Oxygen Transport

Many microorganisms and most animals obtain energy by respiration, the oxidation of organic or inorganic molecules by $O_2$. At 25°C, however, the concentration of dissolved oxygen in water in contact with air is only about 0.25 mM. Because of their high surface area-to-volume ratio, aerobic microorganisms can obtain enough oxygen for respiration by passive diffusion of $O_2$ through the cell membrane. As the size of an organism increases, however, its volume increases much more rapidly than its surface area, and the need for oxygen depends on its volume. Consequently, as a multicellular organism grows larger, its need for $O_2$ rapidly outstrips the supply available through diffusion. Unless a transport system is available to provide an adequate supply of oxygen for the interior cells, organisms that contain more than a few cells cannot exist. In addition, $O_2$ is such a powerful oxidant that the oxidation reactions used to obtain metabolic energy must be carefully controlled to avoid releasing so much heat that the water in the cell boils. Consequently, in higher-level organisms, the respiratory apparatus is located in internal compartments called mitochondria, which are the power plants of a cell. Oxygen must therefore be transported not only to a cell but also to the proper compartment within a cell.

Three different chemical solutions to the problem of oxygen transport have developed independently in the course of evolution, as indicated in Table 22.6.2. Mammals, birds, reptiles, fish, and some insects use a heme protein called hemoglobin to transport oxygen from the lungs to the cells, and they use a related protein called myoglobin to temporarily store oxygen in the tissues. Several classes of invertebrates, including marine worms, use an iron-containing protein called hemerythrin to transport oxygen, whereas other classes of invertebrates (arthropods and mollusks) use a copper-containing protein called hemocyanin. Despite the presence of the hem- prefix, hemerythrin and hemocyanin do not contain a metal–porphyrin complex.

Table 22.6.2: Some Properties of the Three Classes of Oxygen-Transport Proteins

| Protein | Source | M per Subunit | M per $O_2$ Bound | Color (deoxy form) | Color (oxy form) |
|---|---|---|---|---|---|
| hemoglobin | mammals, birds, fish, reptiles, some insects | 1 Fe | 1 Fe | red-purple | red |
| hemerythrin | marine worms | 2 Fe | 2 Fe | colorless | red |
| hemocyanin | mollusks, crustaceans, spiders | 2 Cu | 2 Cu | colorless | blue |

## Myoglobin and Hemoglobin

Myoglobin is a relatively small protein that contains 150 amino acids. The functional unit of myoglobin is an iron–porphyrin complex that is embedded in the protein (Figure 26.8.1). In myoglobin, the heme iron is five-coordinate, with only a single histidine imidazole ligand from the protein (called the proximal histidine because it is near the iron) in addition to the four nitrogen atoms of the porphyrin. A second histidine imidazole (the distal histidine because it is more distant from the iron) is located on the other side of the heme group, too far from the iron to be bonded to it. Consequently, the iron atom has a vacant coordination site, which is where $O_2$ binds.

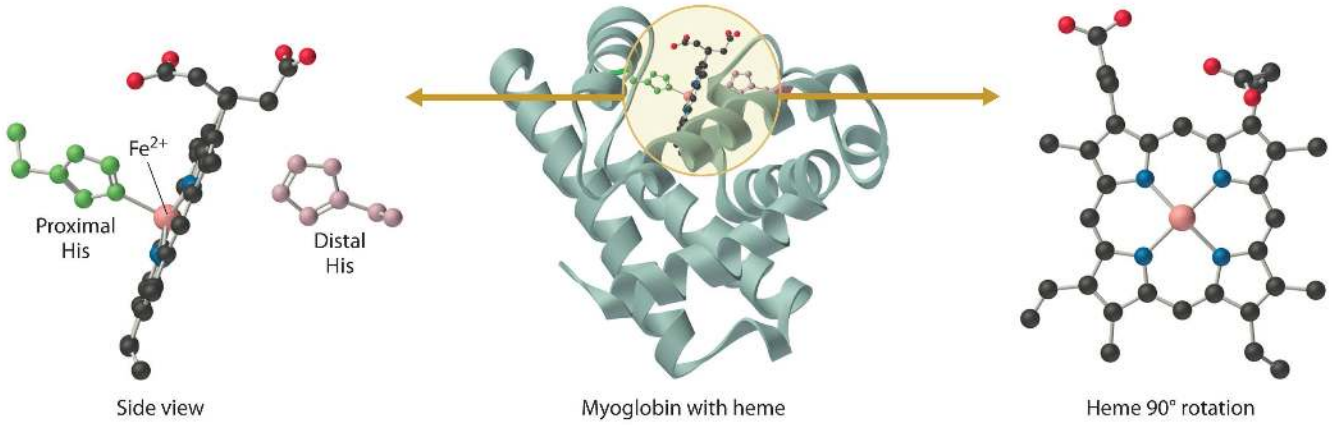



Figure 22.6.6: The Structure of Deoxymyoglobin, Showing the Heme Group. The iron in deoxymyoglobin is five-coordinate, with one histidine imidazole ligand from the protein. Oxygen binds at the vacant site on iron.

In the ferrous form (deoxymyoglobin), the iron is five-coordinate and high spin. Because high-spin $Fe^{2+}$ is too large to fit into the "hole" in the center of the porphyrin, it is about 60 pm above the plane of the porphyrin. When $O_2$ binds to deoxymyoglobin to form oxymyoglobin, the iron is converted from five-coordinate (high spin) to six-coordinate (low spin; Figure 26.8.2). Because low-spin $Fe^{2+}$ and $Fe^{3+}$ are smaller than high-spin $Fe^{2+}$, the iron atom moves into the plane of the porphyrin ring to form an octahedral complex. The $O_2$ pressure at which half of the molecules in a solution of myoglobin are bound to $O_2$ ($P_{1/2}$) is about 1 mm Hg ($1.3 \times 10^{-3}$ atm).

> *A vacant coordination site at a metal center in a protein usually indicates that a small molecule will bind to the metal ion, whereas a coordinatively saturated metal center is usually involved in electron transfer.*

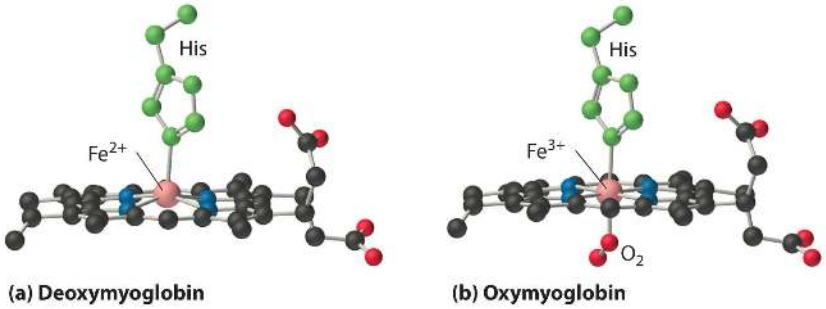



Figure 22.6.7: Oxygen Binding to Myoglobin and Hemoglobin. (a) The $Fe^{2+}$ ion in deoxymyoglobin is high spin, which makes it too large to fit into the "hole" in the center of the porphyrin. (b) When $O_2$ binds to deoxymyoglobin, the iron is converted to low-spin $Fe^{3+}$, which is smaller, allowing the iron to move into the plane of the four nitrogen atoms of the porphyrin to form an octahedral complex.

Hemoglobin consists of two subunits of 141 amino acids and two subunits of 146 amino acids, both similar to myoglobin; it is called a tetramer because of its four subunits. Because hemoglobin has very different $O_2$-binding properties, however, it is not simply a "super myoglobin" that can carry four $O_2$ molecules simultaneously (one per heme group). The shape of the $O_2$-binding curve of myoglobin (Mb; Figure 22.6.7) can be described mathematically by the following equilibrium:

$$MbO_2 \rightleftharpoons Mb + O_2 \tag{22.6.2}$$

$$K_{diss} = \frac{[Mb][O_2]}{[MbO_2]} \tag{22.6.3}$$

In contrast, the $O_2$-binding curve of hemoglobin is S shaped (Figure 22.6.8). As shown in the curves, at low oxygen pressures, the affinity of deoxyhemoglobin for $O_2$ is substantially lower than that of myoglobin, whereas at high $O_2$ pressures the two proteins have comparable $O_2$ affinities. The physiological consequences of the unusual S-shaped $O_2$-binding curve of hemoglobin are enormous. In the lungs, where $O_2$ pressure is highest, the high oxygen affinity of deoxyhemoglobin allows it to be completely loaded with $O_2$, giving four $O_2$ molecules per hemoglobin. In the tissues, however, where the oxygen pressure is much lower, the decreased oxygen affinity of hemoglobin allows it to release $O_2$, resulting in a net transfer of oxygen to myoglobin.

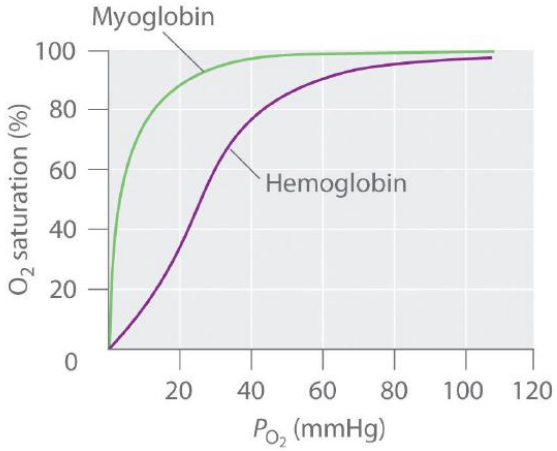



Figure 22.6.8: The $O_2$-Binding Curves of Myoglobin and Hemoglobin. The curve for myoglobin can be described by a simple equilibrium between deoxy- and oxymyoglobin, but the S-shaped curve for hemoglobin can be described only in terms of a cooperative interaction between the four hemes.

The S-shaped $O_2$-binding curve of hemoglobin is due to a phenomenon called cooperativity, in which the affinity of one heme for $O_2$ depends on whether the other hemes are already bound to $O_2$. Cooperativity in hemoglobin requires an interaction between the four heme groups in the hemoglobin tetramer, even though they are more than 3000 pm apart, and depends on the change in structure of the heme group that occurs with oxygen binding. The structures of deoxyhemoglobin and oxyhemoglobin are slightly different, and as a result, deoxyhemoglobin has a much lower $O_2$ affinity than myoglobin, whereas the $O_2$ affinity of oxyhemoglobin is essentially identical to that of oxymyoglobin. Binding of the first two $O_2$ molecules to deoxyhemoglobin causes

the overall structure of the protein to change to that of oxyhemoglobin; consequently, the last two heme groups have a much higher affinity for $O_2$ than the first two.

Oxygen is not unique in its ability to bind to a ferrous heme complex; small molecules such as CO and NO bind to deoxymyoglobin even more tightly than does $O_2$. The interaction of the heme iron with oxygen and other diatomic molecules involves the transfer of electron density from the filled $t_{2g}$ orbitals of the low-spin $d^6$ $Fe^{2+}$ ion to the empty π* orbitals of the ligand. In the case of the $Fe^{2+}$–$O_2$ interaction, the transfer of electron density is so great that the Fe–$O_2$ unit can be described as containing low-spin $Fe^{3+}$ ($d^5$) and $O_2^-$. We can therefore represent the binding of $O_2$ to deoxyhemoglobin and its release as a reversible redox reaction:

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{3+}{-}O_2^- \tag{22.6.4}$$

As shown in Figure 22.6.9, the Fe–$O_2$ unit is bent, with an Fe–O–O angle of about 130°. Because the π* orbitals in CO are empty and those in NO are singly occupied, these ligands interact more strongly with $Fe^{2+}$ than does $O_2$, in which the π* orbitals of the neutral ligand are doubly occupied.

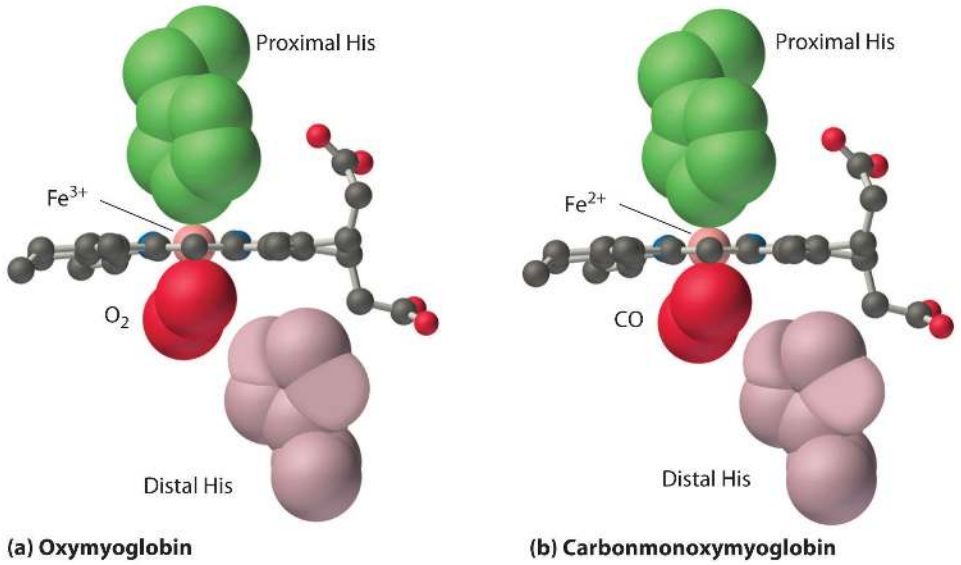



Figure 22.6.9: Binding of $O_2$ and CO to the Iron of Myoglobin. Because the Fe–O–O unit is bent, while the Fe–C–O unit is linear, the imidazole group of the distal histidine in hemoglobin interferes with CO binding and decreases the affinity of hemoglobin for CO.

Although CO has a much greater affinity for a ferrous heme than does $O_2$ (by a factor of about 25,000), the affinity of CO for deoxyhemoglobin is only about 200 times greater than that of $O_2$, which suggests that something in the protein is decreasing its affinity for CO by a factor of about 100. Both CO and NO bind to ferrous hemes in a linear fashion, with an Fe–C(N)–O angle of about 180°, and the difference in the preferred geometry of $O_2$ and CO provides a plausible explanation for the difference in affinities. As shown in Figure 22.6.9, the imidazole group of the distal histidine is located precisely where the oxygen atom of bound CO would be if the Fe–C–O unit were linear. Consequently, CO cannot bind to the heme in a linear fashion; instead, it is forced to bind in a bent mode that is similar to the preferred structure for the Fe–$O_2$ unit. This results in a significant decrease in the affinity of the heme for CO, while leaving the $O_2$ affinity unchanged, which is important because carbon monoxide is produced continuously in the body by degradation of the porphyrin ligand (even in nonsmokers). Under normal conditions, CO occupies approximately 1% of the heme sites in hemoglobin and myoglobin. If the affinity of hemoglobin and myoglobin for CO were 100 times greater (due to the absence of the distal histidine), essentially 100% of the heme sites would be occupied by CO, and no oxygen could be transported to the tissues. Severe carbon-monoxide poisoning, which is frequently fatal, has exactly the same effect. Thus the primary function of the distal histidine appears to be to decrease the CO affinity of hemoglobin and myoglobin to avoid self-poisoning by CO.

### Hemerythrin

Hemerythrin is used to transport $O_2$ in a variety of marine invertebrates. It is an octamer (eight subunits), with each subunit containing two iron atoms and binding one molecule of $O_2$. Deoxyhemerythrin contains two $Fe^{2+}$ ions per subunit and is colorless, whereas oxyhemerythrin contains two $Fe^{3+}$ ions and is bright reddish violet. These invertebrates also contain a monomeric form of hemerythrin that is located in the tissues, analogous to myoglobin. The binding of oxygen to hemerythrin and its release can be described by the following reaction, where the $HO_2^-$ ligand is the hydroperoxide anion derived by the deprotonation of hydrogen peroxide ($H_2O_2$):

$$2\,Fe^{2+} + O_2 + H^+ \rightleftharpoons 2\,Fe^{3+}{-}O_2H \tag{22.6.5}$$

Thus $O_2$ binding is accompanied by the transfer of two electrons (one from each $Fe^{2+}$) and a proton to $O_2$.

### Hemocyanin

Hemocyanin is used for oxygen transport in many arthropods (spiders, crabs, lobsters, and centipedes) and in mollusks (shellfish, octopi, and squid); it is responsible for the bluish-green color of their blood. The protein is a polymer of subunits that each contain two copper atoms (rather than iron), with an aggregate molecular mass of greater than 1,000,000 amu. Deoxyhemocyanin contains two $Cu^+$ ions per subunit and is colorless, whereas oxyhemocyanin contains two $Cu^{2+}$ ions and is bright blue. As with hemerythrin, the binding and release of $O_2$ correspond to a two-electron reaction:

$$2\,Cu^+ + O_2 \rightleftharpoons Cu^{2+}{-}{O_2}^{2-}{-}Cu^{2+} \tag{22.6.6}$$

Although hemocyanin and hemerythrin perform the same basic function as hemoglobin, these proteins are not interchangeable. In fact, hemocyanin is so foreign to humans that it is one of the major factors responsible for the common allergies to shellfish.

> *Myoglobin, hemoglobin, hemerythrin, and hemocyanin all use a transition-metal complex to transport oxygen.*

## Enzymes Involved in Oxygen Activation

Many of the enzymes involved in the biological reactions of oxygen contain metal centers with structures that are similar to those used for $O_2$ transport. Many of these enzymes also contain metal centers that are used for electron transfer, which have structures similar to those of the electron-transfer proteins discussed previously. In this section, we briefly describe two of the most important examples: dioxygenases and methane monooxygenase.

Dioxygenases are enzymes that insert both atoms of $O_2$ into an organic molecule. In humans, dioxygenases are responsible for cross-linking collagen in connective tissue and for synthesizing complex organic molecules called prostaglandins, which trigger inflammation and immune reactions. Iron is by far the most common metal in dioxygenases; and the target of the most commonly used drug in the world, aspirin, is an iron enzyme that synthesizes a specific prostaglandin. Aspirin inhibits this enzyme by binding to the iron atom at the active site, which prevents oxygen from binding.

Methane monooxygenase catalyzes the conversion of methane to methanol. The enzyme is a monooxygenase because only one atom of $O_2$ is inserted into an organic molecule, while the other is reduced to water:

$$CH_4 + O_2 + 2\,e^- + 2\,H^+ \rightarrow CH_3OH + H_2O \tag{22.6.7}$$

Because methane is the major component of natural gas, there is enormous interest in using this reaction to convert methane to a liquid fuel (methanol) that is much more convenient to ship and store. Because the C–H bond in methane is one of the strongest C–H bonds known, however, an extraordinarily powerful oxidant is needed for this reaction. The active site of methane monooxygenase contains two Fe atoms that bind $O_2$, but the details of how the bound $O_2$ is converted to such a potent oxidant remain unclear.

## Metal Ions as Lewis Acids

Reactions catalyzed by metal ions that do not change their oxidation states during the reaction are usually group transfer reactions, in which a group such as the phosphoryl group ($-PO_3^{2-}$) is transferred. These enzymes usually use metal ions such as $Zn^{2+}$, $Mg^{2+}$, and $Mn^{2+}$, and they range from true metalloenzymes, in which the metal ion is tightly bound, to metal-activated enzymes, which

require the addition of metal ions for activity. Because tight binding is usually the result of specific metal–ligand interactions, metalloenzymes tend to be rather specific for a particular metal ion. In contrast, the binding of metal ions to metal-activated enzymes is largely electrostatic in nature; consequently, several different metal ions with similar charges and sizes can often be used to give an active enzyme.

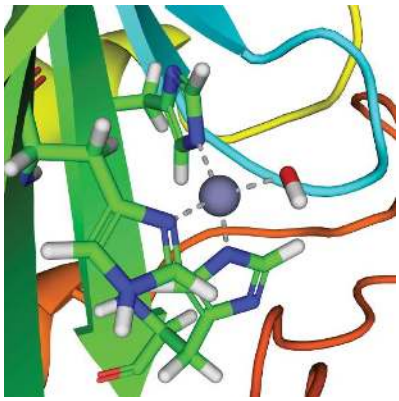
> *Metalloenzymes generally contain a specific metal ion, whereas metal-activated enzymes can use any of several metal ions of similar size and charge.*

A metal ion that acts as a Lewis acid can catalyze a group transfer reaction in many different ways, but we will focus on only one of these, using a zinc enzyme as an example. Carbonic anhydrase is found in red blood cells and catalyzes the reaction of $CO_2$ with water to give carbonic acid.

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{22.6.8}$$

Although this reaction occurs spontaneously in the absence of a catalyst, it is too slow to absorb all the $CO_2$ generated during respiration. Without a catalyst, tissues would explode due to the buildup of excess $CO_2$ pressure. Carbonic anhydrase contains a single $Zn^{2+}$ ion per molecule, which is coordinated by three histidine imidazole ligands and a molecule of water. Because $Zn^{2+}$ is a Lewis acid, the $pK_a$ of the $Zn^{2+}$–$OH_2$ unit is about 8 versus 14 for pure water. Thus at pH 7–8, a significant fraction of the enzyme molecules contain the $Zn^{2+}$–$OH^-$ group, which is much more reactive than bulk water. When carbon dioxide binds in a nonpolar site next to the $Zn^{2+}$–$OH^-$ unit, it reacts rapidly to give a coordinated bicarbonate ion that dissociates from the enzyme:

$$Zn^{2+}\!-\!OH^- + CO_2 \rightleftharpoons Zn^{2+}\!-\!OCO_2H^- \rightleftharpoons Zn^{2+} + HCO_3^- \tag{22.6.9}$$



*The active site of carbonic anhydrase.*

Thus the function of zinc in carbonic anhydrase is to generate the hydroxide ion at pH 7.0, far less than the pH required in the absence of the metal ion.

## Enzymes That Use Metals to Generate Organic Radicals

An organic radical is an organic species that contains one or more unpaired electrons. Chemists often consider organic radicals to be highly reactive species that produce undesirable reactions. For example, they have been implicated in some of the irreversible chemical changes that accompany aging. It is surprising, however, that organic radicals are also essential components of many important enzymes, almost all of which use a metal ion to generate the organic radical within the enzyme. These enzymes are involved in the synthesis of hemoglobin and DNA, among other important biological molecules, and they are the targets of pharmaceuticals for the treatment of diseases such as anemia, sickle-cell anemia, and cancer. In this section, we discuss one class of radical enzymes that use vitamin $B_{12}$.

Vitamin $B_{12}$ was discovered in the 1940s as the active agent in the cure of pernicious anemia, which does not respond to increased iron in the diet. Humans need only tiny amounts of vitamin $B_{12}$, and the average blood concentration in a healthy adult is only about $3.5 \times 10^{-8}$ M. The structure of vitamin $B_{12}$, shown in Figure 22.6.10, is similar to that of a heme, but it contains cobalt instead of iron, and its structure is much more complex. In fact, vitamin $B_{12}$ has been called the most complex nonpolymeric biological

molecule known and was the first naturally occurring organometallic compound to be isolated. When vitamin $B_{12}$ (the form present in vitamin tablets) is ingested, the axial cyanide ligand is replaced by a complex organic group.

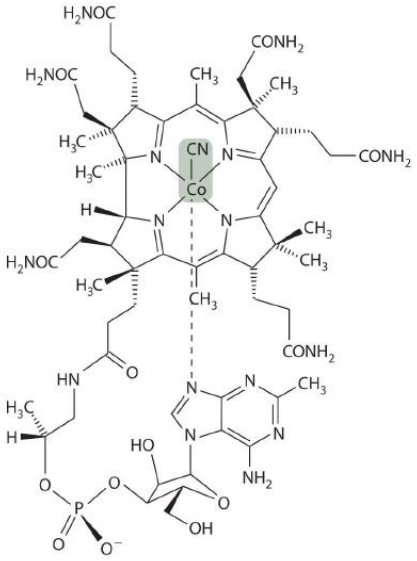
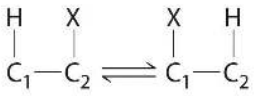



Figure 22.6.10: Vitamin $B_{12}$ In the body, the axial cyanide ligand found in the vitamin is replaced by a complex organic unit. Heterolytic cleavage of the Co–C bond in the resulting organometallic complex generates an organic radical for the catalysis of rearrangement reactions.

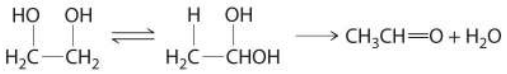
The cobalt–carbon bond in the enzyme-bound form of vitamin $B_{12}$ and related compounds is unusually weak, and it is particularly susceptible to homolytic cleavage:

$$\mathrm{CoCH_2R} \rightleftharpoons \mathrm{Co^{2+\cdot}} + \cdot\mathrm{CH_2R} \tag{22.6.10}$$

Homolytic cleavage of the $Co^{3+}$–$CH_2R$ bond produces two species, each of which has an unpaired electron: a $d^7$ $Co^{2+}$ derivative and an organic radical, $\cdot CH_2R$, which is used by vitamin $B_{12}$-dependent enzymes to catalyze a wide variety of reactions. Virtually all vitamin $B_{12}$-catalyzed reactions are rearrangements in which an H atom and an adjacent substituent exchange positions:




In the conversion of ethylene glycol to acetaldehyde, the initial product is the hydrated form of acetaldehyde, which rapidly loses water:




The enzyme uses the $\cdot CH_2R$ radical to temporarily remove a hydrogen atom from the organic substrate, which then rearranges to give a new radical. Transferring the hydrogen atom back to the rearranged radical gives the product and regenerates the $\cdot CH_2R$ radical.

The metal is not involved in the actual catalytic reaction; it provides the enzyme with a convenient mechanism for generating an organic radical, which does the actual work. Many examples of similar reactions are now known that use metals other than cobalt to generate an enzyme-bound organic radical.

> *Nearly all vitamin $B_{12}$-catalyzed reactions are rearrangements that occur via a radical reaction.*

## Summary

Three separate steps are required for organisms to obtain essential transition metals from their environment: mobilization of the metal, transport of the metal into the cell, and transfer of the metal to where it is needed within a cell or an organism. The process of iron uptake is best understood. To overcome the insolubility of $Fe(OH)_3$, many bacteria use organic ligands called siderophores, which have high affinity for Fe(III) and are secreted into the surrounding medium to increase the total concentration of dissolved iron. The iron–siderophore complex is absorbed by a cell, and the iron is released by reduction to Fe(II). Mammals use the low pH of the stomach to increase the concentration of dissolved iron. Iron is absorbed in the intestine, where it forms an Fe(III) complex with a protein called transferrin that is transferred to other cells for immediate use or storage in the form of ferritin.

Proteins that contain one or more tightly bound metal ions are called metalloproteins, and metalloproteins that catalyze biochemical reactions are called metalloenzymes. Proteins that transfer electrons from one place to another are called electron-transfer proteins. Most electron-transfer proteins are metalloproteins, such as iron–sulfur proteins, cytochromes, and blue copper proteins that accept and donate electrons. The oxidized and reduced centers in all electron-transfer proteins have similar structures to ensure that electron transfer to and from the metal occurs rapidly. Metalloproteins also use the ability of transition metals to bind small molecules, such as $O_2$, $N_2$, and $H_2$, to transport or catalyze the reactions of these small molecules. For example, hemoglobin, hemerythrin, and hemocyanin, which contain heme iron, nonheme iron, and copper, respectively, are used by different kinds of organisms to bind and transfer $O_2$. Other metalloenzymes use transition-metal ions as Lewis acids to catalyze group transfer reactions. Finally, some metalloenzymes use homolytic cleavage of the cobalt–carbon bond in derivatives of vitamin $B_{12}$ to generate an organic radical that can abstract a hydrogen atom and thus cause molecular rearrangements to occur.

## Key Takeaway

- Organisms have developed strategies to extract transition metals from the environment and use the metals in electron-transfer reactions, reactions of small molecules, Lewis-acid catalysis, and the generation of reactive organic radicals.

## Conceptual Problems

1. What are the advantages of having a metal ion at the active site of an enzyme?
2. Why does the structure of the metal center in a metalloprotein that transfers electrons show so little change after oxidation or reduction?

## Structure and Reactivity

1. In enzymes, explain how metal ions are particularly suitable for generating organic radicals.
2. A common method for treating carbon-monoxide poisoning is to have the patient inhale pure oxygen. Explain why this treatment is effective.

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# CHAPTER OVERVIEW

## 23: Organic Compounds

Carbon is unique among the elements in its ability to catenate, to form a wide variety of compounds that contain long chains and/or rings of carbon atoms. Some of the most complex chemical structures known are those of the organic molecules found in living organisms. In spite of their size and complexity, these biological molecules obey the same chemical principles as simpler organic molecules.


23.1: Organic Compounds
23.2: Functional Groups and Classes of Organic Compounds
23.3: Isomers of Organic Compounds
23.4: Reactivity of Organic Molecules
23.5: Common Classes of Organic Reactions
23.6: Common Classes of Organic Compounds
23.7: The Molecules of Life

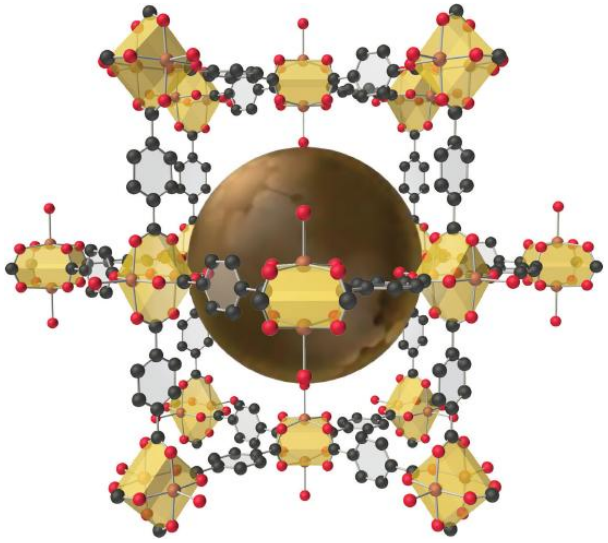

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# 23.1: Organic Compounds

**Learning Objectives**

- To understand the difference between organic and inorganic molecules

Organic substances have been used throughout this text to illustrate the differences between ionic and covalent bonding and to demonstrate the intimate connection between the structures of compounds and their chemical reactivity. You learned, for example, that even though NaOH and alcohols (ROH) both have OH in their formula, NaOH is an ionic compound that dissociates completely in water to produce a basic solution containing $Na^+$ and $OH^-$ ions, whereas alcohols are covalent compounds that do not dissociate in water and instead form neutral aqueous solutions. You also learned that an amine ($RNH_2$), with its lone pairs of electrons, is a base, whereas a carboxylic acid ($RCO_2H$), with its dissociable proton, is an acid.



The structure of a solid with a hybrid metal-organic framework. Organic and inorganic groups of the proper structure can be used to synthesize solids with very large pores (central sphere) that can accommodate a variety of small molecules. The rigid benzene rings are used as “props” to hold the metal units (carboxylate-bridged copper dimers) apart. Such solids have potential applications in hydrogen storage for use in fuel cells or automobiles.

Carbon is unique among the elements in its ability to catenate, to form a wide variety of compounds that contain long chains and/or rings of carbon atoms. Some of the most complex chemical structures known are those of the organic molecules found in living organisms. In spite of their size and complexity, these biological molecules obey the same chemical principles as simpler organic molecules. Thus we can use Lewis electron structures to understand the preferred mode of reactivity of a variety of organic compounds, relative electronegativities and bond polarities to predict how certain groups of atoms will react, and molecular orbital theory to explain why certain organic species that contain multiple bonds are especially stable or undergo particular reactions when they interact with light. In this chapter, we continue our description of organic compounds by focusing on their molecular structures and reactivity; we will also introduce some of the fundamental types of reactions and reaction mechanisms you will encounter in organic and biological chemistry. We discuss why butter is a solid and oils are liquids despite the apparent similarities in their structures, why the widely used anti-inflammatory drug ibuprofen takes longer than half an hour to relieve pain, and the identity of the major carcinogen in grilled meats and cigarette smoke. The chapter concludes with a brief introduction to the molecules of life, which will explain how the consumption of lactose can result in mental retardation and cirrhosis of the liver in some individuals, how hibernating animals survive during the winter, and how certain groups of antibiotics kill bacteria that are harmful to humans.

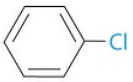
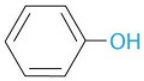
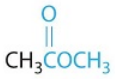
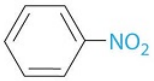
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# 23.2: Functional Groups and Classes of Organic Compounds

**Learning Objectives**

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as $CO_2H$). The major families of organic compounds are characterized by their functional groups. Figure 23.2.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

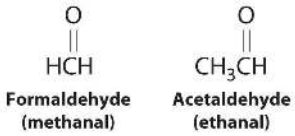
| Class | General Formula | Example | Common Name (Systematic Name) | Common Suffix/Prefix (Systematic) |
|---|---|---|---|---|
| **Hydrocarbons** | | | | |
| Alkanes | RH | $CH_3CH_3$ | ethane | -ane |
| Alkenes | $RR'C{=}CR''R'''$ | $H_2C{=}CH_2$ | ethylene (ethene) | -ene |
| Alkynes | $RC{\equiv}CR'$ | $HC{\equiv}CH$ | acetylene (ethyne) | (-yne) |
| Arenes | ArH[a] |  | benzene | -ene |
| **Halogen-Containing Compounds** | | | | |
| Alkyl halides | RX | $CH_3CH_2Cl$ | ethyl chloride (chloroethane) | halide (halo-) |
| Aryl halides | ArX[a] |  | chlorobenzene | halo- |
| **Oxygen-Containing Compounds** | | | | |
| Alcohols | ROH[a] | $CH_3CH_2OH$ | ethyl alcohol (ethanol) | -ol |
| Phenols | ArOH[b] |  | phenol | -ol |
| Ethers | ROR′ | $H_3CH_2COCH_2CH_3$ | diethyl ether | ether |
| Aldehydes | RCHO |  | acetaldehyde (ethanal) | -aldehyde (-al) |
| Ketones | RR′C=O |  | acetone (2-propanone) | -one |
| Carboxylic acids | $RCO_2H$ |  | acetic acid (ethanoic acid) | -ic acid (-oic acid) |
| **Carboxylic Acid Derivatives** | | | | |
| Esters | $RCO_2R'$ |  | methyl acetate (methyl ethanoate) | -ate (-oate) |
| Amides | RCONHR′ |  | *N*-methylacetamide | -amide |
| **Nitrogen-Containing Compounds** | | | | |
| Amines | $RNH_2$, RNHR′, RNR′R″ | $CH_3CH_2NH_2$ | ethylamine | -amine |
| Nitriles | $RC{\equiv}N$ | $H_3CC{\equiv}N$ | acetonitrile | -nitrile |
| Nitro compounds | $ArNO_2$[a] |  | nitrobenzene | nitro- |


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[a]R indicates an alkyl group [b]Ar indicates an aryl group Figure 23.2.1: Major Classes of Organic Compounds

The first family listed in Figure 23.2.1 is the hydrocarbons. These include alkanes, with the general molecular formula $C_nH_{2n+2}$ where n is an integer; alkenes, represented by $C_nH_{2n}$; alkynes, represented by $C_nH_{2n-2}$; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.




Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first $CH_3$ group in dimethyl benzene is indicated with a 1, but the second $CH_3$ group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 23.2.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the $CH_3$ groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para- compounds, the name is meta-xylene or m-xylene.

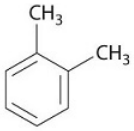
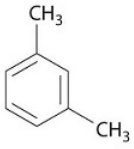
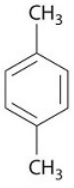
| Prefix | Positions of Methyl Groups | Example | Common Name (Systematic Name) |
|---|---|---|---|
| *ortho-* | 1,2 |  | *o*-xylene (1,2-dimethylbenzene) |
| *meta-* | 1,3 |  | *m*-xylene (1,3-dimethylbenzene) |
| *para-* | 1,4 |  | *p*-xylene (1,4-dimethylbenzene) |

Figure 23.2.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

## Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

## Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

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# 23.3: Isomers of Organic Compounds

**Learning Objectives**

- To learn how organic compounds with the same molecular formula can have different three-dimensional structures.

In earlier discussions of organic compounds, we focused on differences in how the functional groups were connected to the carbon framework. Differences in connectivity resulted in different chemical compounds with different names. You learned, for example, that although 1-propanol (*n*-propanol) and 2-propanol (isopropanol) have the same molecular formula ($C_3H_8O$), they have different physical and chemical properties. Just as with metal complexes, compounds that have the same molecular formula but different arrangements of atoms are called isomers. (For more information on metal complexes, see Section 21.4.) In this section, we describe various types of isomers, beginning with those whose three-dimensional structures differ only as the result of rotation about a C–C bond.

## Conformational Isomers

The C–C single bonds in ethane, propane, and other alkanes are formed by the overlap of an $sp^3$ hybrid orbital on one carbon atom with an $sp^3$ hybrid orbital on another carbon atom, forming a σ bond (Figure 23.2.1). Each $sp^3$ hybrid orbital is cylindrically symmetrical (all cross-sections are circles), resulting in a carbon–carbon single bond that is also cylindrically symmetrical about the C–C axis. Because rotation about the carbon–carbon single bond can occur without changing the overlap of the $sp^3$ hybrid orbitals, there is no significant electronic energy barrier to rotation. Consequently, many different arrangements of the atoms are possible, each corresponding to different degrees of rotation. Differences in three-dimensional structure resulting from rotation about a σ bond are called differences in *conformation*, and each different arrangement is called a conformational isomer (or conformer)Isomers whose three-dimensional structures differ because of rotation about a σ bond..

### Note the Pattern

Conformational isomers differ in their three-dimensional structure due to rotation about a σ bond.

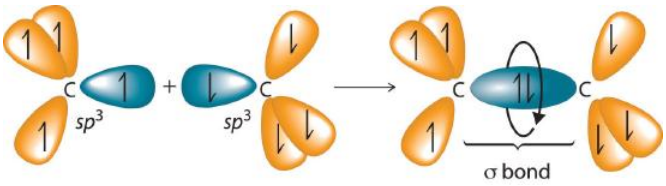



Figure 23.2.1 Carbon–Carbon Bonding in **Alkanes** Overlapping $sp^3$ hybrid orbitals on adjacent carbon atoms form a cylindrically symmetrical σ bond. Because rotation about the bond does not affect the overlap of the bonding orbitals, there is no electronic energy barrier to rotation.

The simplest alkane to have a conformational isomer is ethane. Differences between the conformations of ethane are depicted especially clearly in drawings called *Newman projections*, such as those shown in part (a) in Figure 23.2.2 In a Newman projection, the ethane molecule is viewed along the C–C axis, with the carbon that is in front shown as a vertex and the carbon that is in back shown as a circle. The three hydrogen atoms nearest the viewer are shown bonded to the front carbon, and the three hydrogen atoms farthest from the viewer are shown bonded to the circle. In one extreme, called the *eclipsed conformation*, the C–H bonds on adjacent carbon atoms lie in the same plane. In the other extreme, called the *staggered conformation*, the hydrogen atoms are positioned as far from one another as possible. Rotation about the C–C bond produces an infinite number of conformations between these two extremes, but the staggered conformation is the most stable because it minimizes electrostatic repulsion between the hydrogen atoms on adjacent carbons.

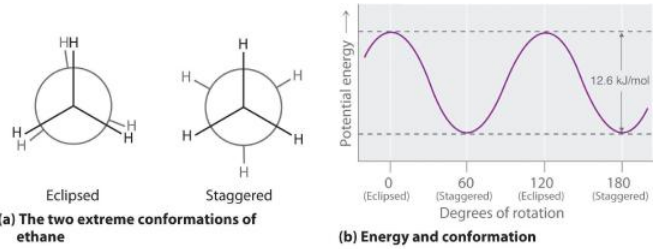



Figure 23.2.2 Eclipsed and Staggered Conformations of Ethane(a) In a Newman projection, the molecule is viewed along a C–C axis. The carbon in front is represented as a vertex, whereas the carbon that is bonded to it is represented as a circle. In ethane, the C–H bonds to each carbon are positioned at 120° from each other. In the fully eclipsed conformation, the C–H bonds on adjacent carbon atoms are parallel and lie in the same plane. In the staggered conformation, the hydrogen atoms are positioned as far apart as possible. (b) The eclipsed conformation is 12.6 kJ/mol higher in energy than the staggered conformation because of electrostatic repulsion between the hydrogen atoms. An infinite number of conformations of intermediate energy exist between the two extremes.

In a Newman projection, the angles between adjacent C–H bonds on the same carbon are drawn at 120°, although H–C–H angles in alkanes are actually tetrahedral angles of 109.5°, which for chains of more than three carbon atoms results in a *kinked* structure. (For more information on bond angles and molecular modeling, see Section 6.3) Despite this three-dimensional inaccuracy, Newman projections are useful for predicting the relative stability of conformational isomers. As shown in part (b) in Figure 23.2.2, the higher energy of the eclipsed conformation represents an energy barrier of 12.6 kJ/mol that must be overcome for rotation about the C–C bond to occur. This barrier is so low, however, that rotation about the C–C bond in ethane is very fast at room temperature and occurs several million times per second for each molecule.

Longer-chain alkanes can also be represented by Newman projections. In more complex alkanes and alkane derivatives, rotation can occur about *each* C–C bond in a molecule. Newman projections are therefore useful for revealing *steric barriers* to rotation at a particular C–C bond due to the presence of bulky substituents. Figure 23.2.3 shows a plot of potential energy versus the angle of rotation about the central C–C bond (between carbon atoms 2 and 3) of *n*-butane ($C_4H_{10}$). The structure that minimizes electrostatic repulsion is the one in which the methyl groups, corresponding to carbon atoms 1 and 4, are as far apart as possible; that is, the staggered conformation. Notice that because the substituents on C2 and C3 in *n*-butane are not all the same, energetically nonequivalent eclipsed and staggered conformations are possible; most molecules interconvert rapidly between these conformations by a series of simple rotations.

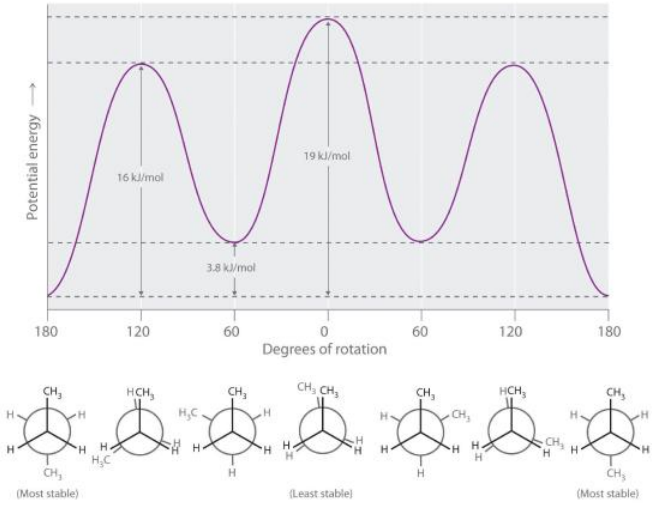



Figure 23.2.3 Potential Energy Plot and Newman Projections of Eclipsed and Staggered Conformations of *n*-Butane In these projections, the molecule is viewed along the C2–C3 axis. The least stable structure is the eclipsed conformation in which the two methyl groups (C1 and C4) are adjacent to each other. The most stable structure is the staggered conformation in which the methyl groups are as far apart as possible. Because the substituents on each central carbon atom are not all the same, a 120° rotation about the C2–C3 bond generates energetically nonequivalent eclipsed and staggered conformations.

### Example 23.2.1

Draw Newman projections showing the staggered and eclipsed conformations of 1,1,1-trichloroethane ($CCl_3CH_3$).

**Given:** organic molecule

**Asked for:** staggered and eclipsed conformations

**Strategy:**

**A** Identify the C–C bond of interest. Then draw the Newman projection by representing one carbon as a vertex and the other as a circle.

**B** Draw bonds to each carbon at 120° angles from one another, with one arrangement representing the staggered conformation and the other the eclipsed conformation.

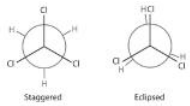
**C** Complete the Newman projections by attaching the appropriate atoms or substituent groups to the central C atoms in each conformation.

**Solution:**

**A** There is only one C–C bond: C1 is connected to three Cl atoms and C2 to three H atoms. We draw C1 as a point and C2 as a circle.

**B** Now we draw bonds on each carbon at 120° angles from one another to represent the staggered conformation and the eclipsed conformation.

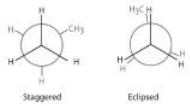
**C** We then attach the H and Cl atoms to the carbon atoms in each conformation as shown.




Exercise

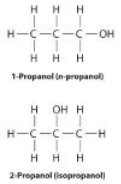
Draw Newman projections to illustrate the staggered and eclipsed conformations of propane ($C_3H_8$) as viewed along the C1–C2 axis.

**Answer**

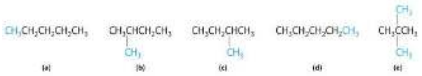



## Structural Isomers

Unlike conformational isomers, which do not differ in connectivity, structural isomersIsomers that have the same molecular formula but differ in which atoms are bonded to one another. differ in connectivity, as illustrated here for 1-propanol and 2-propanol. (For more information on structural isomers, see Section 21.4.) Although these two alcohols have the same molecular formula ($C_3H_8O$), the position of the –OH group differs, which leads to differences in their physical and chemical properties.




In the conversion of one structural isomer to another, *at least one bond must be broken and reformed at a different position in the molecule*. Consider, for example, the following five structures represented by the formula $C_5H_{12}$:



Of these structures, (a) and (d) represent the same compound, as do (b) and (c). No bonds have been broken and reformed; the molecules are simply rotated about a 180° vertical axis. Only three—*n*-pentane (a) and (d), 2-methylbutane (b) and (c), and 2,2-dimethylpropane (e)—are structural isomers. Because no bonds are broken in going from (a) to (d) or from (b) to (c), these alternative representations are not structural isomers. The three structural isomers—either (a) or (d), either (b) or (c), and (e)—have distinct physical and chemical properties.

### Note the Pattern

Structural isomers differ in their connectivity.

### Example 23.2.2

Draw all the structural isomers of $C_6H_{14}$.

**Given:** organic molecule

**Asked for:** all structural isomers

**Strategy:**

**A** Draw the simplest structural isomer, which is often the straight-chain alkane.

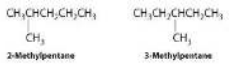
**B** Obtain branched isomers by substituting one hydrogen along the chain with an appropriate group from the chain.

**C** If possible, substitute more than one hydrogen with appropriate groups to obtain isomers that are more highly branched.

**Solution:**

**A** The simplest structural isomer is the straight-chain alkane *n*-hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$).

**B** Removing a methyl group from one end and reattaching it to adjacent carbons while substituting hydrogen in its place give two other structures:



**C** To obtain yet another structural isomer, move two methyl groups to create a molecule with two branches:



We create one more structural isomer by attaching two methyl groups to the same carbon atom:

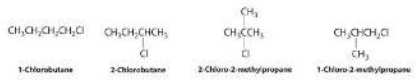


Thus there are four structural isomers of $C_6H_{14}$.

Exercise

Draw all the structural isomers of $C_4H_9Cl$.

**Answer**



## Stereoisomers

Molecules with the same connectivity but different arrangements of the atoms in space are called stereoisomersMolecules that have the same connectivity but whose component atoms have different orientations in space.. There are two types of stereoisomers:

geometric and optical. *Geometric isomers* differ in the relative position(s) of substituents in a rigid molecule. (For more information on stereoisomers, see Section 21.4) Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement (part (a) in Figure 6.4.4). Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either *cis* or *trans*, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, *cis* and *trans* isomers are actually two distinct chemical compounds.

### Note the Pattern

Stereoisomers have the same connectivity but different arrangements of atoms in space.

*Optical isomers* are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have *identical physical properties*, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be *chiral* (pronounced “ky-ral,” from the Greek *cheir*, meaning “hand”). Examples of some familiar chiral objects are your hands, feet, and ears. As shown in part (a) in Figure 23.2.4, your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An *achiral* object is one that *can* be superimposed on its mirror image, as shown by the superimposed flasks in part (b) in Figure 23.2.4

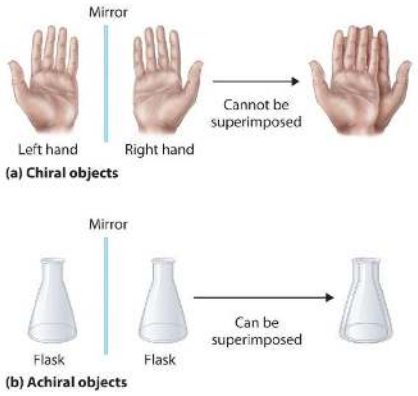



Figure 23.2.4 Chiral and Achiral Objects (a) Objects that are nonsuperimposable mirror images of each other are chiral, such as the left and the right hand. (b) The unmarked flask is achiral because it can be superimposed on its mirror image.

Most chiral organic molecules have at least one carbon atom that is bonded to four different groups, as occurs in the bromochlorofluoromethane molecule shown in part (a) in Figure 23.2.5 This carbon, often designated by an asterisk in structural drawings, is called a *chiral center* or *asymmetric carbon atom*. If the bromine atom is replaced by another chlorine (part (b) in Figure 23.2.5), the molecule and its mirror image can now be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Asymmetric carbon atoms are found in many naturally occurring molecules, such as lactic acid, which is present in milk and muscles, and nicotine, a component of tobacco. A molecule and its nonsuperimposable mirror image are called *enantiomers* (from the Greek *enantiou*, meaning “opposite”).

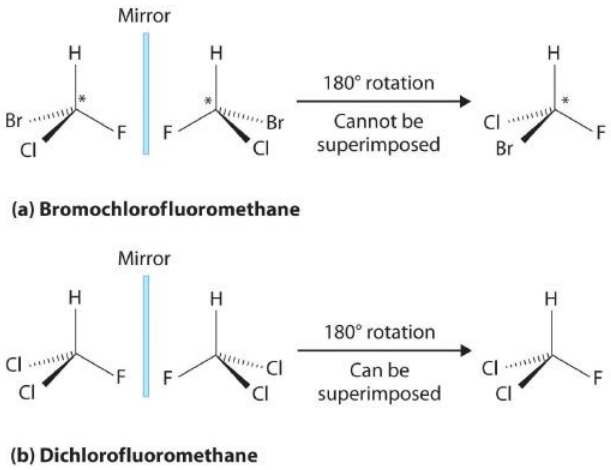



Figure 23.2.5 Comparison of Chiral and Achiral Molecules (a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.



## Example 23.2.3

Draw the *cis* and *trans* isomers of each compound.

1. 1,3-dimethylcyclopentane
2. 3,4-dichloro-3-hexene

**Given:** organic compounds

**Asked for:** *cis* and *trans* isomers

**Strategy:**

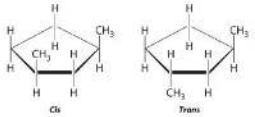
Draw the unsubstituted compound corresponding to the systematic name given. Then place substituents on the same side to obtain the *cis* isomer and on opposite sides to obtain the *trans* isomer.

**Solution:**

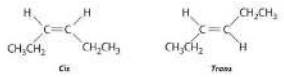
1. The name tells us that this compound contains a five-carbon ring with two methyl groups attached. The 1,3 notation means that the methyl groups are not adjacent in the five-membered ring:



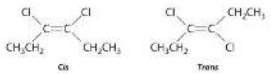
   Placing the methyl substituents on the same side of the ring gives the *cis* isomer, whereas placing them on opposite sides of the ring gives the *trans* isomer:



2. The compound 3-hexene can exist as a *cis* or *trans* isomer:



Replacing the hydrogen atoms on the third and fourth carbons by chlorine does not change the overall structures of the isomers:

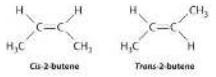
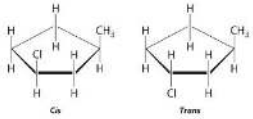


Exercise

Draw the *cis* and *trans* isomers of each compound.

1. 2-butene
2. 1-methyl-3-chlorocyclopentane

**Answer**

1. 
2. 

## Example 22.3.4

Which of these compounds exist as at least one pair of enantiomers?

1. 
2. 
3. 
4. 

**Given:** organic compounds

**Asked for:** existence of enantiomers

**Strategy:**

Determine whether the compound is chiral. In most cases, this means that at least one carbon is bonded to four different groups. If the compound is chiral, it exists as enantiomers.

**Solution:**

1. The carbons in $–CH_3$ and $–CH_2–$ are each bound to more than one hydrogen, so they are achiral. The central carbon is bound to two identical ethyl groups, so it is also achiral. Because there are no chiral centers in this compound, it has no enantiomers.
2. All carbons are bonded to at least two H atoms except for the one bonded to Br, which is bonded to four different groups: –Br, $–CH_3$, –H, and $–CH_2CH_3$. The compound therefore has one chiral center and, as a result, exists as enantiomers: the structure shown and its nonsuperimposable mirror image.
3. The carbons in each $–CH_3$ are bonded to more than one hydrogen, so they are achiral. One carbon is bonded to two $–CH_3$ groups, making it achiral also. This compound has no enantiomers.
4. One carbon is bonded to three hydrogens and one to two oxygens, so they are achiral. The central carbon is bonded to four different groups: $–CH_3$, –H, $–NH_2$, and $–CO_2H$, so it is chiral, and the compound has two enantiomers.

Exercise

Which of these compounds have at least one pair of enantiomers?

1.
2. 
3. 
4. 

**Answer**

(c)

## Optical Activity of Enantiomers

Although enantiomers have identical densities, melting and boiling points, colors, and solubility in most solvents, they differ in their interaction with *plane-polarized light*, which consists of electromagnetic waves oscillating in a single plane. In contrast, normal (unpolarized) light consists of electromagnetic waves oscillating in all directions perpendicular to the axis of propagation. When normal light is passed through a substance called a polarizer, only light oscillating in one direction is transmitted. A polarizer selectively filters out light that oscillates in any but the desired plane (Figure 23.2.6).

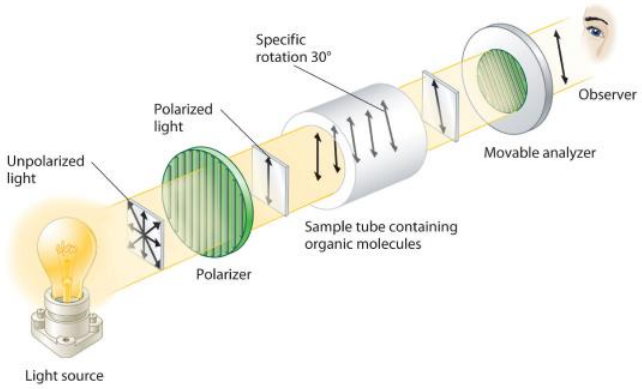



Figure 23.2.6 Detecting the Optical Activity of Chiral **Substances** When polarized light is passed through a solution that contains an achiral compound, there is no net rotation of the plane of polarization of the light. In contrast, when polarized light is passed through a solution that contains one enantiomer of a chiral compound, as shown here, the light is rotated either clockwise [*dextrorotatory*, (+) enantiomer] or counterclockwise [*levorotatory*, (−) enantiomer] by an angle that depends on the molecular structure and concentration of the compound, the path length, and the wavelength of the light.

When plane-polarized light is passed through a solution, electromagnetic radiation interacts with the solute and solvent molecules. If the solution contains an achiral compound, the plane-polarized light enters and leaves the solution unchanged because achiral molecules cause it to rotate in random directions. The solute is therefore said to be *optically inactive*. If the solution contains a single enantiomer of a chiral compound, however, the plane-polarized light is rotated in only one direction, and the solute is said to be *optically active*. A clockwise rotation is called *dextrorotatory* (from the Latin *dextro*, meaning “to the right”) and is indicated in the name of the compound by (+), whereas a counterclockwise rotation is called *levorotatory* (from the Latin *levo*, meaning “to the left”) and is designated (−). As you will soon discover, this designation is important in understanding how chiral molecules interact with one another.

### Note the Pattern

Chiral molecules are optically active; achiral molecules are not.

The magnitude of the rotation of plane-polarized light is directly proportional to the number of chiral molecules in a solution; it also depends on their molecular structure, the temperature, and the wavelength of the light. Because of these variables, every chiral compound has a specific rotationThe amount (in degrees) by which the plane of polarized light is rotated when the light is passed through a solution that contains 1.0 g of a solute per 1.0 mL of solvent in a tube 10.0 cm long., which is defined as the amount (in degrees) by which the plane of polarized light is rotated when the light is passed through a solution containing 1.0 g of solute per 1.0 mL of solvent in a tube 10.0 cm long. A chiral solution that contains equal concentrations of a pair of enantiomers is called a

*racemic mixture*. In such a solution, the optical rotations exactly cancel one another, so there is no net rotation, and the solution is optically inactive. The categories of stereoisomers are summarized in Figure 23.2.7 .

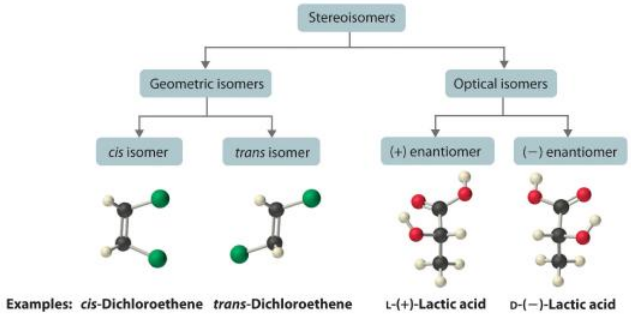
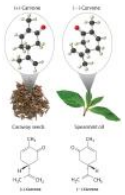



Figure 23.2.7 Classification of **Stereoisomers** In both types of stereoisomer—geometric and optical—isomeric molecules have identical connectivity, but the arrangement of atoms in space differs. *Cis* and *trans* isomers exhibit different physical and chemical properties, whereas enantiomers differ only in their interaction with plane-polarized light and reactions in asymmetric environments. Depending on the direction in which they rotate polarized light, enantiomers are identified as (+) or (−). The designations L- and D- represent an alternative labeling system.

## Interactions of Enantiomers with Other Chiral Molecules

In living organisms, virtually every molecule that contains a chiral center is found as a single enantiomer, not a racemic mixture. At the molecular level, our bodies are chiral and interact differently with the individual enantiomers of a particular compound. For example, the two enantiomers of carvone produce very different responses in humans: (−)-carvone is the substance responsible for the smell of spearment oil, and (+)-carvone—the major flavor component of caraway seeds—is responsible for the characteristic aroma of rye bread.



A pharmaceutical example of a chiral compound is ibuprofen, a common analgesic and anti-inflammatory agent that is the active ingredient in pain relievers such as Motrin and Advil (Figure 23.5.2). The drug is sold as a racemic mixture that takes approximately 38 minutes to achieve its full effect in relieving pain and swelling in an adult human. Because only the (+) enantiomer is active in humans, however, the same mass of medication would relieve symptoms in only about 12 minutes if it consisted of only the (+) enantiomer. Unfortunately, isolating only the (+) enantiomer would substantially increase the cost of the drug. Conversion of the (−) to (+) enantiomer in the human body accounts for the delay in feeling the full effects of the drug. A racemic mixture of another drug, the sedative thalidomide, was sold in Europe from 1956 to the early 1960s. It was prescribed to treat nausea during pregnancy, but unfortunately only the (+) enantiomer was safe for that purpose. The (−) enantiomer was discovered to be a relatively potent *teratogen*, a substance that causes birth defects, which caused the children of many women who had taken thalidomide to be born with missing or undeveloped limbs. As a result, thalidomide was quickly banned for this use. It is currently used to treat leprosy, however, and it has also shown promise as a treatment for AIDS (acquired immunodeficiency syndrome).

These examples dramatically illustrate the point that the biological activities of enantiomers may be very different. But how can two molecules that differ only by being nonsuperimposable mirror images cause such different responses? The biological effects of many substances—including molecules such as carvone that have a scent and drugs such as ibuprofen and thalidomide—depend on their interaction with chiral sites on specific receptor proteins. As schematically illustrated in Figure 23.2.8, only one enantiomer of a chiral substance interacts with a particular receptor, thereby initiating a response. The other enantiomer may not bind at all, or it may bind to *another* receptor, producing a different response.

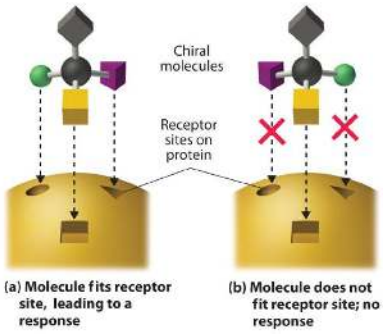



Figure 23.2.8 The Interaction of Chiral Molecules with Biological **Receptors**Only one enantiomer of a chiral molecule fits into a chiral receptor site, which typically is a small portion of a large protein. The binding of a molecule to its receptor elicits a characteristic response. The other enantiomer cannot fit into the same site and thus elicits no response. It may, however, produce a different response by binding to another site.

## Summary

**Isomers** are different compounds that have the same molecular formula. For an organic compound, rotation about a σ bond can produce different three-dimensional structures called **conformational isomers (or conformers)**. In a Newman projection, which represents the view along a C–C axis, the eclipsed conformation has the C–H bonds on adjacent carbon atoms parallel to each other and in the same plane, representing one conformational extreme. In the staggered conformation, the opposite extreme, the hydrogen atoms are as far from one another as possible. Electrostatic repulsions are minimized in the staggered conformation. **Structural isomers** differ in the connectivity of the atoms. Structures that have the same connectivity but whose components differ in their orientations in space are called **stereoisomers**. Stereoisomers can be geometric isomers, which differ in the placement of substituents in a rigid molecule, or optical isomers, nonsuperimposable mirror images. Molecules that are nonsuperimposable mirror images are chiral molecules. A molecule and its nonsuperimposable mirror image are called enantiomers. These differ in their interaction with plane-polarized light, light that oscillates in only one direction. A compound is optically active if its solution rotates plane-polarized light in only one direction and optically inactive if its rotations cancel to produce no net rotation. A clockwise rotation is called dextrorotatory and is indicated in the compound's name by (+), whereas a counterclockwise rotation is called levorotatory, designated by (−). The **specific rotation** is the amount (in degrees) by which the plane of polarized light is rotated when light is passed through a solution containing 1.0 g of solute per 1.0 mL of solvent in a tube 10.0 cm long. A solution that contains equal concentrations of each enantiomer in a pair is a racemic mixture; such solutions are optically inactive.

## Key Takeaways

- Isomers can be conformational or structural.
- Stereoisomers have the same connectivity but can be optical or geometric isomers.

## Conceptual Problems

1. What hybrid orbitals are used to form C–C bonds in saturated hydrocarbons? Describe the bond.
2. How are conformational isomers related? Sketch two conformational isomers of propane, looking along the C1–C2 axis.
3. Why do alkanes with more than two carbons have a kinked structure? Explain why a kinked structure is so stable.
4. Are *n*-pentane and 2-methylbutane conformational isomers or structural isomers? How would you separate these compounds from a mixture of the two?
5. How are structural isomers different from stereoisomers? Do stereoisomers have free rotation about all carbon–carbon bonds? Explain your answers.
6. Which of these objects is chiral?
    1. a shoe
    2. a laced football
    3. an automobile
    4. a fork

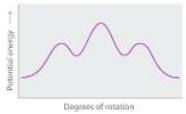
7. Which of these objects is chiral?
    1. a rollerblade
    2. an unmarked baseball bat
    3. a bicycle
    4. your arms
    5. a spoon
8. Are all stereoisomers also enantiomers? Are all enantiomers stereoisomers? Explain your answers.

## Answers

1. $sp^3$; it is a σ bond that is cylindrically symmetrical (all cross sections perpendicular to the internuclear axis are circles).
2. 
3. The $sp^3$ hybridized orbitals form bonds at tetrahedral angles (109.5°), which forces the carbon atoms to form a zigzag chain.
4. 
5. 
6. 
7. (a), (c), and (d)
8. 

## Structure and Reactivity

1. Single bonds between carbon atoms are free to rotate 360°.
    1. Explain what happens to the potential energy of an *n*-hexane molecule as rotation occurs around the C2–C3 bond.
    2. Draw Newman projections of the *n*-hexane conformations corresponding to the energy minima and maxima in the diagram, which shows potential energy versus degrees of rotation about the C3–C4 axis.

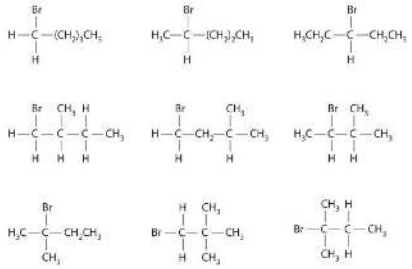
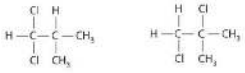
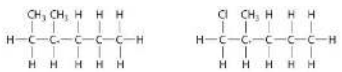



2. Sketch all the structural isomers of each compound.
    1. $C_6H_{13}Br$
    2. $C_3H_6Cl_2$
3. Draw all the possible structural isomers of each compound.
    1. $C_5H_{11}Br$
    2. $C_4H_8Cl_2$
4. Sketch all the isomers of each compound. Identify the *cis*- and *trans*-isomers.
    1. monochlorobutene
    2. bromochloropropene
5. Which molecules are chiral? On the structural formulas of the chiral molecules, identify any chiral centers with an asterisk.
    1. 2,2-dimethylpentane
    2. 1,2-dimethylpentane
    3. 2,4-dimethylpentane
    4. 1-chloro-2-methylpentane
6. Which molecules are chiral? On the structural formulas of the chiral molecules, identify any chiral centers with an asterisk.
    1. 1,1-dichloropropane
    2. 1,2-dichloropropane

3. 1,3-dichloropropane
4. 1,1,2-trichloropropane

7. Draw the structures of the enantiomers of each compound.
   1. $CH_2CHCHClBr$
   2. 4-chloro-2-hexene
   3. methylethylpropylamine
8. Draw the structures of the enantiomers of each compound.
   1. 4-methyl-2-hexene
   2. methylethylhexylamine
   3. $CH_3CH_2CH(CH_3)Cl$
9. Draw the structures of the enantiomers of each compound.
   1. 
   2. 
10. Draw the structures of the enantiomers of each compound.
    1. 
    2. 
    3. 

## Answers

1.
2.
3. 1. 
   2. 
4.
5. (b) and (d);
   
6.

7.
8.
9.
10.

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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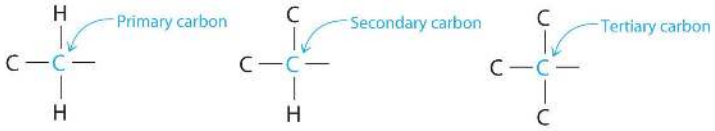
# 23.4: Reactivity of Organic Molecules

**Learning Objectives**

- To understand the relationship between structure and reactivity for a series of related organic compounds.

Understanding why organic molecules react as they do requires knowing something about the structure and properties of the transient species that are generated during chemical reactions. Identifying transient intermediates enables chemists to elucidate reaction mechanisms, which often allows them to control the products of a reaction. In designing the synthesis of a molecule, such as a new drug, for example, chemists must be able to understand the mechanisms of intermediate reactions to maximize the yield of the desired product and minimize the occurrence of unwanted reactions. Moreover, by recognizing the common reaction mechanisms of simple organic molecules, we can understand how more complex systems react, including the much larger molecules encountered in biochemistry.

Nearly all chemical reactions, whether organic or inorganic, proceed because atoms or groups of atoms having a positive charge or a partial positive charge interact with atoms or groups of atoms having a negative charge or a partial negative charge. Thus when a bond in a hydrocarbon is cleaved during a reaction, identifying the transient species formed, some of which are charged, allows chemists to determine the mechanism and predict the products of a reaction.




Chemists often find that the reactivity of a molecule is affected by the degree of substitution of a carbon that is bonded to a functional group. These carbons are designated as primary, secondary, or tertiary. A primary carbon is bonded to only one other carbon and a functional group, a secondary carbon is bonded to two other carbons and a functional group, and a tertiary carbon is bonded to three other carbons and a functional group.

## Reactive Intermediates

Cleaving a C–H bond can generate either $–C^+$ and $H^–$, $–C·$ and $H·$ or $–C^–$ and $H^+$, all of which are unstable and therefore highly reactive. The most common species formed is $–C^+$, which is called a *carbocation* (part (a) in Figure 24.3.1). A carbocation has only six valence electrons and is therefore electron deficient. It is an *electrophile* (from "electron" and the Greek suffix phile, meaning "loving"), which is a species that needs electrons to complete its octet. (Recall that electron-deficient compounds, such as those of the group 13 elements, act as Lewis acids in inorganic reactions.) In general, when a highly electronegative atom, such as Cl, is bonded to a carbocation, it draws electrons away from the carbon and destabilizes the positive charge. In contrast, alkyl groups and other species stabilize the positive charge by increasing electron density at the carbocation. Thus a tertiary carbocation ($R_3C^+$) is more stable than a primary carbocation ($RCH_2^+$).

> *The reactivity of a molecule is often affected by the degree of substitution of the carbon bonded to a functional group.*

Adding one electron to a carbocation produces a neutral species called a radical. An example is the methyl radical ($·CH_3$), shown in part (b) in Figure 24.3.1. Because the carbon still has less than an octet of electrons, it is electron deficient and also behaves as an electrophile. Like carbocations, radicals can be stabilized by carbon substituents that can donate some electron density to the electron-deficient carbon center. Like carbocations, a tertiary radical ($R_3C·$) is more stable than a primary radical ($RCH_2·$).

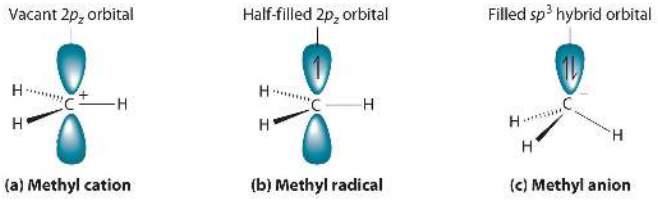



Figure 23.4.1: Transient Intermediates in Organic Reactions. (a) The simplest carbocation is the methyl cation ($CH_3^+$), which has six valence electrons and is an electrophile. Its structure is trigonal planar, with an $sp^2$ hybridized carbon and a vacant p orbital. (b) The methyl radical ($\cdot CH_3$) is a radical that, like the carbocation, is trigonal planar and an electrophile. It is also $sp^2$ hybridized, but there is a single electron in the unhybridized p orbital. (c) The simplest organic carbanion is $CH_3^-$, which has a trigonal pyramidal structure with an $sp^3$ hybridized carbon that has a lone pair of electrons. Because it has a strong tendency to share its lone pair with another atom or molecule, a carbanion is a nucleophile.

Adding an electron to a radical produces a carbanion, which contains a negatively charged carbon with eight valence electrons (part (c) in Figure 24.3.1). The methyl anion ($CH_3^-$) has a structure that is similar to $NH_3$ with its lone pair of electrons, but it has a much stronger tendency to share its lone pair with another atom or molecule. A carbanion is a nucleophile (from “nucleus” and phile), an electron-rich species that has a pair of electrons available to share with another atom. Carbanions are destabilized by groups that donate electrons, so the relationship between their structure and reactivity is exactly the opposite of carbocations and radicals. That is, a tertiary carbanion ($R_3C^-$) is less stable than a primary carbanion ($RCH_2^-$). Carbanions are most commonly encountered in organometallic compounds such as methyllithium ($CH_3Li$) or methylmagnesium chloride ($CH_3MgCl$), where the more electropositive metal ion stabilizes the negative charge on the more electronegative carbon atom.

Electrophiles such as carbocations seek to gain electrons and thus have a strong tendency to react with nucleophiles, which are negatively charged species or substances with lone pairs of electrons. Reacting electrophiles with nucleophiles is a central theme in organic reactions.

> *Electrophiles react with nucleophiles.*

**Example 23.4.1**

Classify each species as an electrophile, a nucleophile, or neither.

a. $BF_3$
b. $CH_4$
c. $(CH_3)_3C^+$
d. $NH_2^-$

**Given**: molecular formulas

**Asked for**: mode of reactivity

**Strategy**:

Determine whether the compound is electron deficient, in which case it is an electrophile; electron rich, in which case it is a nucleophile; or neither.

**Solution**:

a. The $BF_3$ molecule is a neutral compound that contains a group 13 element with three bonds to B. The boron atom has only six valence electrons, so it tends to accept an electron pair. The compound is therefore an electrophile.
b. The $CH_4$ molecule has four bonds to C, which is typical of a neutral group 14 compound. The carbon atom has no lone pairs to share and no tendency to gain electrons, and each hydrogen atom forms one bond that contains two valence electrons. Thus $CH_4$ is neither an electrophile nor a nucleophile.
c. The $(CH_3)_3C^+$ cation contains a group 14 atom (carbon) with only three bonds. It therefore has only six valence electrons and seeks electrons to complete an octet. Hence $(CH_3)_3C^+$, a carbocation, is an electrophile.
d. The $NH_2^-$ anion contains a group 15 element with a lone pair of electrons, two bonds, and a negative charge, giving N a total of eight electrons. With its negative charge, the N atom has two lone pairs of electrons, making it a potent nucleophile.

**? Exercise 23.4.1**

Classify each compound as an electrophile, a nucleophile, or neither.

a. $C_6H_5OH$
b. $AlBr_3$
c. $(CH_3)_4C$

**Answer**:

a. nucleophile
b. electrophile
c. neither

## Summary

Electrophiles have a strong tendency to react with nucleophiles. The reactivity of a molecule is often affected by the degree of substitution of the carbon bonded to a functional group; the carbon is designated as primary, secondary, or tertiary. Identifying the transient species formed in a chemical reaction, some of which are charged, enables chemists to predict the mechanism and products of the reaction. One common transient species is a carbocation, a carbon with six valence electrons that is an electrophile; that is, it needs electrons to complete its octet. A radical is a transient species that is neutral but electron deficient and thus acts as an electrophile. In contrast, a carbanion has eight valence electrons and is negatively charged. It is an electron-rich species that is a nucleophile because it can share a pair of electrons. In chemical reactions, electrophiles react with nucleophiles.

## Conceptual Problems

1. Arrange $CH_2F^+$, $CHCl_2^+$, $CH_3^+$, and $CHF_2^+$ in order of increasing stability. Explain your reasoning.
2. Arrange $CH_3CH_2^+$, $CHBr_2^+$, $CH_3^+$, and $CHBrCl^+$ in order of decreasing stability. Explain your reasoning.
3. Identify the electrophile and the nucleophile in each pair.
    a. $CH_3^-$ and $Li^+$
    b. $CH_3ONa$ and formaldehyde
    c. $H^+$ and propene
    d. benzene and $Cl^-$
4. Identify the electrophile and the nucleophile in each pair.
    a. $CH_3^+$ and $Br^-$
    b. HC≡CNa and pentanal
    c. acetone and $CN^-$
    d. $(CH_3)_2S$ and $CH_3I$

## Answers

1. $CHF_2^+ < CHCl_2^+ < CH_2F^+ < CH_3^+$; electronegative substituents destabilize the positive charge. The greater the number of electronegative substituents and the higher their electronegativity, the more unstable the carbocation.

3.
    a. $CH_3^-$, nucleophile; $Li^+$, electrophile
    b. $CH_3O^-$, nucleophile; formaldehyde, electrophile
    c. $H^+$, electrophile; propene, nucleophile
    d. benzene, electrophile; $Cl^-$, nucleophile

## Structure and Reactivity

1. Draw Lewis electron structures of the products of carbon–hydrogen cleavage reactions. What is the charge on each species?
2. Identify the electrophile and the nucleophile in each reaction; then complete each chemical equation.
    a. $CH_3^+ + Cl^- \rightarrow$

b. $CH_3CH{=}CH_2 + HBr \rightarrow$

c. $(CH_3)_3N + BCl_3 \rightarrow$

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# 23.5: Common Classes of Organic Reactions

**Learning Objectives**

- To become familiar with the common classes of organic reactions.

Certain patterns are encountered repeatedly in organic reactions, many reflecting the interactions of nucleophiles and electrophiles. In this section, we discuss five common types of organic reactions: substitution reactions, elimination reactions, addition reactions, radical reactions, and oxidation–reduction reactions. You have encountered many of these types of reactions previously, such as the formation of peptides by the elimination of water, the oxidation–reduction reactions that generate voltage in batteries, and chain reactions that involve organic radicals. (For more information on peptide formation, see Section 12.8. For more information on batteries, see Chapter 19 . For more information on radicals, see Section 14.6.) In this section, we expand our discussion to include some of the mechanisms behind these reactions.

## Substitution

In a substitution reactionA chemical reaction in which one atom or a group of atoms in a substance is replaced by another atom or a group of atoms from another substance., one atom or a group of atoms in a substance is replaced by another atom or group of atoms from another substance. A typical substitution reaction is reacting the hydroxide ion with methyl chloride:

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

Methyl chloride has a polar C–Cl bond, with the carbon atom having a partial positive charge. In Equation 24.1, the electronegative Cl atom is replaced by another electronegative species that is a stronger nucleophile, in this case $OH^-$. Reactions of this sort are called *nucleophilic substitution reactions*. For this type of reaction to occur, the nucleophilic reactant must possess a pair of electrons and have a greater affinity for the electropositive carbon atom than the original substituent.

One type of nucleophilic substitution reaction is shown in Equation 24.1. It proceeds by a mechanism in which the lone pair of electrons on the entering nucleophile ($OH^-$) attacks the partially positively charged carbon atom of the polar C–Cl bond, causing the C–Cl bond to weaken and break:

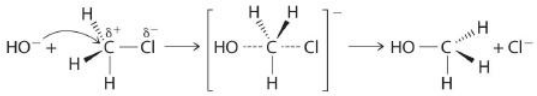
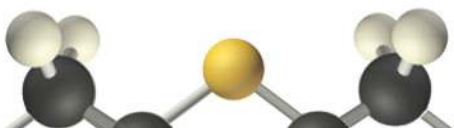


Figure 23.4.1

### Note the Pattern

In nucleophilic substitution reactions, the nucleophile must possess a pair of electrons and have a greater affinity for the electropositive species than the original substituent.

The convention for writing such a mechanism is to draw arrows showing the direction of electron flow—that is, from the electron-rich center (the nucleophile) to the electron-poor center (the electrophile). The intermediate species, enclosed by square brackets, represents a transient arrangement of atoms that is only postulated to exist. If the atom under attack (in this case, the partially positively charged carbon atom) had $–CH_3$ groups bonded to it rather than H atoms, the bulky methyl groups would interfere with the attack by $OH^-$, making the reaction *sterically hindered*. The reaction would then proceed in two discrete steps in a second type of substitution reaction: the C–Cl bond would break, forming the $(CH_3)_3C^+$ carbocation (the electrophile), which would then react with hydroxide (the nucleophile) in a separate step to give the product, $(CH_3)_3COH$.



**Mustard gas.**

An example of a nucleophilic substitution reaction involves the chemical warfare agent known as *mustard gas* [$(ClCH_2CH_2)_2S$], which caused about 400,000 casualties during World War I. Mustard gas is toxic because it contains a chloride that can be displaced by nucleophilic amino groups in proteins, thereby allowing the molecule to irreversibly bond to a protein. Because the other product of the reaction is HCl, mustard gas causes severe burns to mucous membranes in the respiratory tract. If mustard gas reacts with DNA (deoxyribonucleic acid), cross-linking of the DNA strands through sulfur occurs, which results in coding errors, the inhibition of replication, and disruption of other DNA functions. If mustard gas reacts with RNA (ribonucleic acid), protein synthesis is altered (see Section 22.6).

## Elimination

Some reactions involve the removal, or "elimination," of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions, resulting in the formation of a multiple bond and a small molecule.. They have the general form

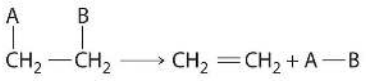



Figure 23.4.2

and are similar to cleavage reactions in inorganic compounds. (For more information on cleavage reactions, see Section 7.5.) A typical example is the conversion of ethyl chloride to ethylene:

$$CH_3CH_2Cl \rightarrow CH_2 = CH_2 + HCl$$

### Note the Pattern

Elimination reactions are similar to cleavage reactions in inorganic compounds.

Much of the approximately 26 million tons of ethylene produced per year in the United States is used to synthesize plastics, such as polyethylene. In Equation 23.4.2, the A–B molecule eliminated is HCl, whose components are eliminated as $H^+$ from the carbon atom on the left and $Cl^-$ from the carbon on the right. When an acid is produced, as occurs here, the reaction is generally carried out in the presence of a base (such as NaOH) to neutralize the acid.

## Addition

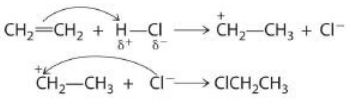
A reaction in which the components of a species A–B are added to adjacent atoms across a carbon–carbon multiple bond is called an addition reactionA chemical reaction in which the components of a species A–B are added to adjacent atoms across a carbon-carbon multiple bond.. An example is the reverse of the reaction shown in Equation 24.2, reacting HCl with ethylene to give ethyl chloride:

$$CH_2 = CH_2 + HCl \rightarrow CH_3CH_2Cl$$

### Note the Pattern

An addition reaction is the reverse of an elimination reaction.

Although a multiple bond is stronger than a single bond, the π bonds of the multiple bond are weaker than the σ bond. The high electron density located between multiply bonded carbon atoms, however, causes alkenes and alkynes to behave like nucleophiles, where nucleophilic attack occurs from the more weakly bound π electrons. Hence alkenes and alkynes are regarded as functional groups. Nucleophilic attack occurs on the $H^{\delta+}$ atom of the polar HCl bond, initially producing a species with a carbon that has only three bonds, a carbocation. In a second nucleophilic attack, $Cl^-$, the electrophile in Equation 23.4.3 attacks the carbocation:



Alcohols, an important class of organic compounds, are often produced by addition reactions. Initial attack by the π bond of an alkene on a $H^{\delta+}$ of $H_3O^+$ produces a carbocation. The carbocation then undergoes nucleophilic attack by a lone pair of electrons from $H_2O$ followed by elimination of $H^+$ to form the alcohol.

## Radical Reactions

Many important organic reactions involve radicals, such as the combustion of fuels. Probably the best known is reacting a saturated hydrocarbon, such as ethane, with a halogen, such as $Br_2$. The overall reaction is as follows:

$$CH_3CH_3 + Br_2 \xrightarrow[or\,h\nu]{400^\circ C} CH_3CH_2Br + HBr$$

Radical chain reactions occur in three stages: *initiation*, *propagation*, and *termination*. (For more information on radicals, see Section 14.6.) At high temperature or in the presence of light, the relatively weak Br–Br bond is broken in an initiation step that produces an appreciable number of Br atoms (Br·). During propagation, a bromine atom attacks ethane, producing a radical, which then reacts with another bromine molecule to produce ethyl bromide:

$$\begin{array}{ll} \cancel{Br\cdot} + CH_3CH_3 & \rightarrow \cancel{CH_3CH_2\cdot} + HBr \\ \cancel{CH_3CH_2\cdot} + Br_2 & \rightarrow CH_3CH_2Br + \cancel{Br\cdot} \\ \text{---------} & \text{----------} \\ Br_2 + CH_3CH_3 & \rightarrow CH_3CH_2Br + HBr \end{array}$$

The sum of the two propagation steps corresponds to the balanced chemical equation for the overall reaction. There are three possible termination steps: the combination of (1) two bromine atoms, (2) two ethyl radicals, or (3) an ethyl and a bromine radical:

$$\begin{array}{cc} Br\cdot + Br\cdot & \rightarrow Br_2 \\ CH_3CH_2\cdot + \cdot CH_2CH_3 & \rightarrow CH_3CH_2CH_2CH_3 \\ CH_3CH_2\cdot + Br\cdot & \rightarrow CH_3CH_2Br \end{array}$$

Because radicals are powerful nucleophiles and hence highly reactive, such reactions are not very selective. For example, the chlorination of *n*-butane gives a roughly 70:30 mixture of 2-chlorobutane, formed from the more stable radical by reacting a secondary carbon and 1-chlorobutane.

### Note the Pattern

Because radicals are highly reactive, radical reactions are usually not very selective.

## Oxidation–Reduction Reactions

**Oxidation–reduction reactions**, which are common in organic chemistry, can often be identified by changes in the number of oxygen atoms at a particular position in the hydrocarbon skeleton or in the number of bonds between carbon and oxygen at that position. An increase in either corresponds to an oxidation, whereas a decrease corresponds to a reduction. Conversely, an increase in the number of hydrogen atoms in a hydrocarbon is often an indication of a reduction. We can illustrate these points by considering how the oxidation state of the carbon atom changes in the series of compounds, which is shown in part (a) in Figure 23.4.3. (For a review of oxidation states and formal changes, see Section 7.5, and Section 8.10). The number of oxygen atoms or the number of bonds to oxygen changes throughout the series. Hence the conversion of methane to formic acid is an oxidation, whereas the conversion of carbon dioxide to methanol is a reduction. Also, the number of hydrogen atoms increases in going from the most oxidized to least oxidized compound. As expected, as the oxidation state of carbon increases, the carbon becomes a more potent electrophile. Thus the carbon of $CO_2$ is a stronger electrophile (i.e., more susceptible to nucleophilic attack) than the carbon of an alkane such as methane.

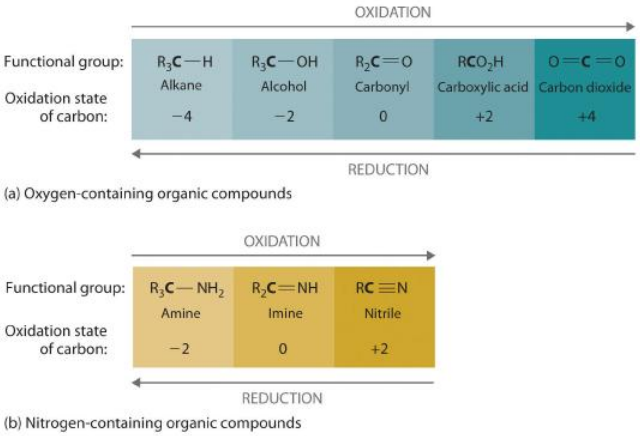



Figure 23.4.3 The Oxidation State of Carbon in Oxygen- and Nitrogen-Containing Functional Groups (a) In a hydrocarbon, oxidation is indicated by an increase in the number of oxygen atoms or carbon–oxygen bonds or a decrease in the number of hydrogen atoms. (b) In nitrogen-containing compounds, the number of carbon–nitrogen bonds changes with the oxidation state of carbon.

Similarly, in compounds with a carbon–nitrogen bond, the number of bonds between the C and N atoms increases as the oxidation state of the carbon increases (part (b) in Figure 23.4.3). In a nitrile, which contains the –C≡N group, the carbon has the same oxidation state (+2) as in a carboxylic acid, characterized by the $–CO_2H$ group. We therefore expect the carbon of a nitrile to be a rather strong electrophile.

## Example 23.4.1

Write an equation to describe each reaction. Identify the electrophile and the nucleophile in each reaction.

1. the nucleophilic substitution reaction of potassium cyanide with 1-chloropropane to give $CH_3CH_2CH_2CN$ (butyronitrile)
2. the electrophilic addition reaction of HBr with *cis*-2-butene

**Given:** reactants, products, and reaction mechanism

**Asked for:** equation and identification of electrophile and nucleophile

**Strategy:**

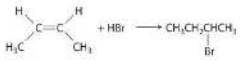
Use the mechanisms described to show how the indicated products are formed from the reactants.

**Solution:**

1. The $CN^-$ ion of KCN is a potent nucleophile that can displace the chlorine atom of 1-chloropropane, releasing a chloride ion. Substitution results in the formation of a new C–C bond: $\underset{}{CN^-} + \underset{1-chloropropane}{CH_3CH_2CH_2Cl} \rightarrow \underset{butylnitrile}{CH_3CH_2CH_2CN} + Cl^-$

   The carbon bonded to chlorine is an electrophile because of the highly polar C–Cl bond.

2. In the electrophilic addition of a hydrogen halide to an alkene, the reaction is as follows:




   The first step is nucleophilic attack of the π electrons of the double bond on the electrophilic hydrogen of the polar H–Br bond to generate the transient carbocation, followed by nucleophilic attack by the halide to give the product. Thus the alkene is the nucleophile, and the proton of the acid is the electrophile.



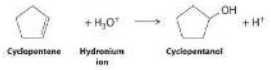

Exercise

Write an equation to describe each reaction. In each reaction, identify the electrophile and nucleophile.

1. the nucleophilic substitution reaction of sodium methoxide ($NaOCH_3$) with benzyl bromide ($C_6H_5CH_2Br$)

2. the acid-catalyzed electrophilic addition reaction of water with cyclopentene

**Answer**

1. $OCH_3^-$ (methoxide ion) + $C_6H_5CH_2Br$ (benzyl bromide) → $C_6H_5CH_2OCH_3$ (benzylmethyl ether) + Br ; $OCH_3^-$ is the nucleophile, and $C_6H_5CH_2Br$ is the electrophile.
2. 


   Cyclopentene is the nucleophile, and $H_3O^+$ is the electrophile.

## Summary

There are common patterns to how organic reactions occur. In a **substitution reaction**, one atom or a group of atoms in a substance is replaced by another atom or a group of atoms from another substance. Bulky groups that prevent attack cause the reaction to be sterically hindered. In an **elimination reaction**, adjacent atoms are removed with subsequent formation of a multiple bond and a small molecule. An **addition reaction** is the reverse of an elimination reaction. Radical reactions are not very selective and occur in three stages: initiation, propagation, and termination. **Oxidation–reduction reactions** in organic chemistry are identified by the change in the number of oxygens in the hydrocarbon skeleton or the number of bonds between carbon and oxygen or carbon and nitrogen.

## Key Takeaway

- The common classes of organic reactions—substitution, elimination, addition, oxidation-reduction, and radical—all involve reacting electrophiles with nucleophiles.

## Conceptual Problems

1. Identify the nucleophile and the electrophile in the nucleophilic substitution reaction of 2-bromobutane with KCN.
2. Identify the nucleophile and the electrophile in the nucleophilic substitution reaction of 1-chloropentane with sodium methoxide.
3. Do you expect an elimination reaction to be favored by a strong or a weak base? Why?
4. Why do molecules with π bonds behave as nucleophiles when mixed with strong electrophiles?

## Answer

1. $CN^-$ is the nucleophile, and $C_2H_5C^{\delta+}HBrCH_3$ is the electrophile.
2. 
3. 
4. 

## Structure and Reactivity

1. Sketch the mechanism for the nucleophilic substitution reaction of potassium cyanide with iodoethane.
2. Sketch the mechanism for the nucleophilic substitution reaction of NaSH with 1-bromopropane.
3. Sketch the mechanism for the elimination reaction of cyclohexylchloride with potassium ethoxide. Identify the electrophile and the nucleophile in this reaction.
4. What is the product of the elimination reaction of 1-bromo-2-methylpropane with sodium ethoxide?
5. Write the structure of the product expected from the electrophilic addition of HBr to *cis*-3-hexene.
6. Write the structure of the product expected from the electrophilic addition of 1-methylcyclopentene to HBr. Identify the electrophile and the nucleophile, and then write a mechanism for this reaction.
7. Write a synthetic scheme for making propene from propane. After synthesizing propene, how would you make 2-bromopropane?

8. Write a synthetic scheme for making ethylene from ethane. After synthesizing ethylene, how would you make iodoethane?
9. From the high-temperature reaction of $Br_2$ with 3-methylpentane, how many monobrominated isomers would you expect to be produced? Which isomer is produced from the most stable radical?
10. For the photochemical reaction of $Cl_2$ with 2,4-dimethylpentane, how many different monochlorinated isomers would you expect to be produced? Which isomer is produced from the most stable precursor radical?
11. How many different radicals can be formed from the photochemical reaction of $Cl_2$ with 3,3,4-trimethylhexane?
12. How many monobrominated isomers would you expect from the photochemical reaction of $Br_2$ with
    1. isobutene?
    2. 2,2,3-trimethylpentane?
13. Arrange acetone, ethane, carbon dioxide, acetaldehyde, and ethanol in order of increasing oxidation state of carbon.
14. What product(s) do you expect from the reduction of a ketone? the oxidation of an aldehyde?
15. What product(s) do you expect from the reduction of formaldehyde? the oxidation of ethanol?

## Answers

1.
2.
3.
4.
5.
6.
7.
8.
9. four; 3-bromo-3-methylpentane
10.
11. seven
12.
13.
14.
15. methanol; acetaldehyde, followed by acetic acid and finally $CO_2$

## Contributors

- Anonymous

Modified by Joshua B. Halpern

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# 23.6: Common Classes of Organic Compounds

**Learning Objectives**

- To understand the general properties of functional groups and the differences in their reactivity.

The general properties and reactivity of each class of organic compounds is largely determined by its functional groups. In this section, we describe the relationships between structure, physical properties, and reactivity for the major classes of organic compounds. We also show you how to apply these relationships to understand some common reactions that chemists use to synthesize organic compounds.

## Alkanes, Alkenes, and Alkynes

The boiling points of alkanes increase smoothly with increasing molecular mass. They are similar to those of the corresponding alkenes and alkynes because of similarities in molecular mass between analogous structures (Table 23.6.1). In contrast, the melting points of alkanes, alkenes, and alkynes with similar molecular masses show a much wider variation because the melting point strongly depends on how the molecules stack in the solid state. It is therefore sensitive to relatively small differences in structure, such as the location of a double bond and whether the molecule is cis or trans.

Table 23.6.1: Boiling Points (in °C) of Alkanes, Alkenes, and Alkynes of Comparable Molecular Mass

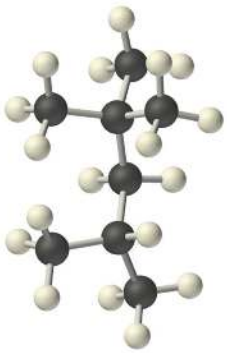
| | Length of Carbon Chain | | |
|---|---|---|---|
| **Class** | **Two C Atoms** | **Three C Atoms** | **Four C Atoms** |
| alkane | −88.6 | −42.1 | −0.5 |
| alkene | −103.8 | −47.7 | −6.3 |
| alkyne | −84.7 | −23.2 | 8.1 |

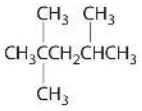
Because alkanes contain only C–C and C–H bonds, which are strong and not very polar (the electronegativities of C and H are similar), they are not easily attacked by nucleophiles or electrophiles. Consequently, their reactivity is limited, and often their reactions occur only under extreme conditions. For example, catalytic cracking can be used to convert straight-chain alkanes to highly branched alkanes, which are better fuels for internal combustion engines. Catalytic cracking is one example of a pyrolysis reaction (from the Greek pyros, meaning “fire,” and lysis, meaning “loosening”), in which alkanes are heated to a sufficiently high temperature to induce cleavage of the weakest bonds: the C–C single bonds. The result is a mixture of radicals derived from essentially random cleavage of the various C–C bonds in the chain. Pyrolysis of n-pentane, for example, is nonspecific and can produce these four radicals:

$$2CH_3CH_2CH_2CH_2CH_3 \xrightarrow{\Delta} CH_3\cdot + CH_2CH_2CH_2\cdot + CH_3CH_2\cdot + CH_3CH_2CH_2\cdot \tag{24.5.1}$$

Recombination of these radicals (a termination step) can produce ethane, propane, butane, n-pentane, n-hexane, n-heptane, and n-octane. Radicals that are formed in the middle of a chain by cleaving a C–H bond tend to produce branched hydrocarbons. In catalytic cracking, lighter alkanes are removed from the mixture by distillation.

Radicals are also produced during the combustion of alkanes, with $CO_2$ and $H_2O$ as the final products. Radicals are stabilized by the presence of multiple carbon substituents that can donate electron density to the electron-deficient carbon. The chemical explanation of octane ratings rests partly on the stability of radicals produced from the different hydrocarbon fuels. Recall that n-heptane, which does not burn smoothly, has an octane rating of 0, and 2,2,4-trimethylpentane (“isooctane”), which burns quite smoothly, has a rating of 100. Isooctane has a branched structure and is capable of forming tertiary radicals that are comparatively stable.

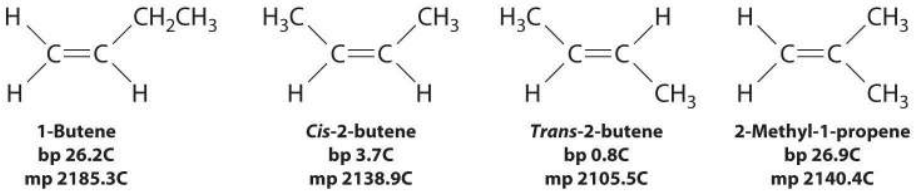




2,2,4-Trimethylpentane
("isooctane")

In contrast, the radicals formed during the combustion of n-heptane, whether primary or secondary, are less stable and hence more reactive, which partly explains why burning n-heptane causes premature ignition and engine knocking.

In Section 24.2, we explained that rotation about the carbon–carbon multiple bonds of alkenes and alkynes cannot occur without breaking a π bond, which therefore constitutes a large energy barrier to rotation (Figure 23.6.1). Consequently, the cis and trans isomers of alkenes generally behave as distinct compounds with different chemical and physical properties. A four-carbon alkene has four possible isomeric forms: three structural isomers, which differ in their connectivity, plus a pair of geometric isomers from one structural isomer (2-butene). These two geometric isomers are cis-2-butene and trans-2-butene. The four isomers have significantly different physical properties.



**1-Butene**
**bp 26.2C**
**mp 2185.3C**

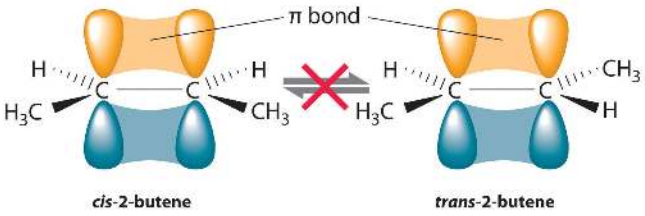
***Cis*-2-butene**
**bp 3.7C**
**mp 2138.9C**

***Trans*-2-butene**
**bp 0.8C**
**mp 2105.5C**

**2-Methyl-1-propene**
**bp 26.9C**
**mp 2140.4C**

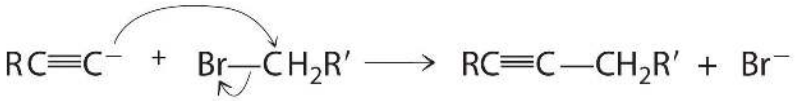
Figure 23.6.1: Carbon–Carbon Bonding in Alkenes and Interconversion of Cis and Trans Isomers

In butane, there is only a small energy barrier to rotation about the C2–C3 σ bond. In the formation of cis- or trans-2-butene from butane, the p orbitals on C2 and C3 overlap to form a π bond. To convert cis-2-butene to trans-2-butene or vice versa through rotation about the double bond, the π bond must be broken. Because this interconversion is energetically unfavorable, cis and trans isomers are distinct compounds that generally have different physical and chemical properties.



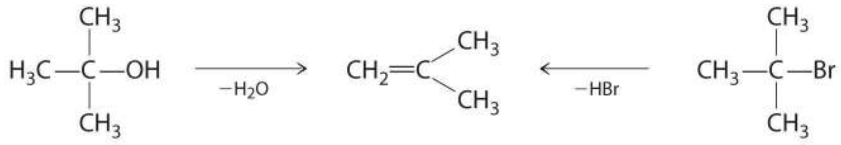

***cis*-2-butene** ***trans*-2-butene**

Alkynes in which the triple bond is located at one end of a carbon chain are called terminal alkynes and contain a hydrogen atom attached directly to a triply bonded carbon: R–C≡C–H. Terminal alkynes are unusual in that the hydrogen atom can be removed relatively easily as $H^+$, forming an acetylide ion ($R–C{\equiv}C^-$). Acetylide ions are potent nucleophiles that are especially useful reactants for making longer carbon chains by a nucleophilic substitution reaction. As in earlier examples of such reactions, the nucleophile attacks the partially positively charged atom in a polar bond, which in the following reaction is the carbon of the Br–C bond:



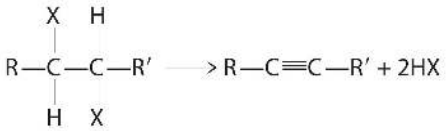

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Alkenes and alkynes are most often prepared by elimination reactions. A typical example is the preparation of 2-methyl-1-propene, whose derivative, 3-chloro-2-methyl-1-propene, is used as a fumigant and insecticide. The parent compound can be prepared from either 2-hydroxy-2-methylpropane or 2-bromo-2-methylpropane:




**2-Hydroxy-2-methylpropane** **2-Methyl-1-propene** **2-Bromo-2-methylpropane**

The reaction on the left proceeds by eliminating the elements of water ($H^+$ plus $OH^-$), so it is a dehydration reaction. If an alkane contains two properly located functional groups, such as –OH or –X, both of them may be removed as $H_2O$ or HX with the formation of a carbon–carbon triple bond:

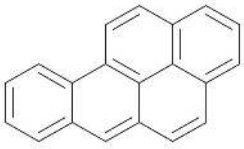



> *Alkenes and alkynes are most often prepared by elimination reactions.*

## Arenes

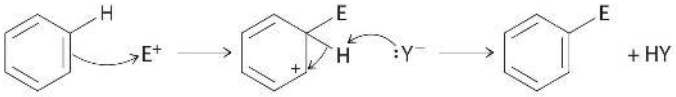
Most arenes that contain a single six-membered ring are volatile liquids, such as benzene and the xylenes, although some arenes with substituents on the ring are solids at room temperature. In the gas phase, the dipole moment of benzene is zero, but the presence of electronegative or electropositive substituents can result in a net dipole moment that increases intermolecular attractive forces and raises the melting and boiling points. For example, 1,4-dichlorobenzene, a compound used as an alternative to naphthalene in the production of mothballs, has a melting point of 52.7°C, which is considerably greater than the melting point of benzene (5.5°C).

Certain aromatic hydrocarbons, such as benzene and benz[a]pyrene, are potent liver toxins and carcinogens. In 1775, a British physician, Percival Pott, described the high incidence of cancer of the scrotum among small boys used as chimney sweeps and attributed it to their exposure to soot. His conclusions were correct: benz[a]pyrene, a component of chimney soot, charcoal-grilled meats, and cigarette smoke, was the first chemical carcinogen to be identified.



**Benz[a]pyrene**

Although arenes are usually drawn with three C=C bonds, benzene is about 150 kJ/mol more stable than would be expected if it contained three double bonds. This increased stability is due to the delocalization of the π electron density over all the atoms of the ring. Compared with alkenes, arenes are poor nucleophiles. Consequently, they do not undergo addition reactions like alkenes; instead, they undergo a variety of electrophilic aromatic substitution reactions that involve the replacement of –H on the arene by a group –E, such as $–NO_2$, $–SO_3H$, a halogen, or an alkyl group, in a two-step process. The first step involves addition of the electrophile (E) to the π system of benzene, forming a carbocation. In the second step, a proton is lost from the adjacent carbon on the ring:




The carbocation formed in the first step is stabilized by resonance.

> *Arenes undergo substitution reactions rather than elimination because of increased stability arising from delocalization of their π electron density.*

Many substituted arenes have potent biological activity. Some examples include common drugs and antibiotics such as aspirin and ibuprofen, illicit drugs such as amphetamines and peyote, the amino acid phenylalanine, and hormones such as adrenaline (Figure 23.6.2).

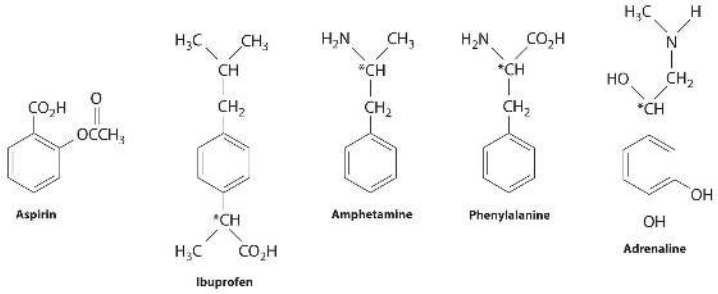



Figure 23.6.2: Biologically Active Substituted Arenes

Aspirin (antifever activity), ibuprofen (antifever and anti-inflammatory activity), and amphetamine (stimulant) have pharmacological effects. Phenylalanine is an amino acid. Adrenaline is a hormone that elicits the "fight or flight" response to stress. Chiral centers are indicated with an asterisk.

## Alcohols and Ethers

Both alcohols and ethers can be thought of as derivatives of water in which at least one hydrogen atom has been replaced by an organic group, as shown here. Because of the electronegative oxygen atom, the individual O–H bond dipoles in alcohols cannot cancel one another, resulting in a substantial dipole moment that allows alcohols to form hydrogen bonds.

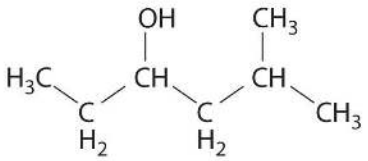



Alcohols therefore have significantly higher boiling points than alkanes or alkenes of comparable molecular mass, whereas ethers, without a polar O–H bond, have intermediate boiling points due to the presence of a small dipole moment (Table 23.6.2). The larger the alkyl group in the molecule, however, the more "alkane-like" the alcohol is in its properties. Because of their polar nature, alcohols and ethers tend to be good solvents for a wide range of organic compounds.

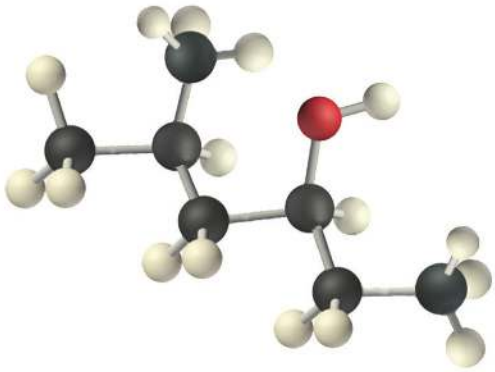
Table 23.6.2: Boiling Points of Alkanes, Ethers, and Alcohols of Comparable Molecular Mass

| | Name | Formula | Molecular Mass (amu) | Boiling Point (°C) |
|---|---|---|---|---|
| **alkane** | propane | $C_3H_8$ | 44 | −42.1 |
| | n-pentane | $C_5H_{12}$ | 72 | 36.1 |
| | n-heptane | $C_7H_{16}$ | 100 | 98.4 |
| **ether** | dimethylether | $(CH_3)_2O$ | 46 | −24.5.1 |
| | diethylether | $(CH_3CH_2)_2O$ | 74 | 34.5 |
| | di-n-propylether | $(CH_3CH_2CH_2)_2O$ | 102 | 90.1 |
| **alcohol** | ethanol | $CH_3CH_2OH$ | 46 | 78.3 |
| | n-butanol | $CH_3(CH_2)_3OH$ | 74 | 117.7 |
| | n-hexanol | $CH_3(CH_2)_5OH$ | 102 | 157.6 |

Alcohols are usually prepared by adding water across a carbon–carbon double bond or by a nucleophilic substitution reaction of an alkyl halide using hydroxide, a potent nucleophile (Figure 23.6.1). Alcohols can also be prepared by reducing compounds that contain the carbonyl functional group (C=O; part (a) in Figure 24.5.7). Alcohols are classified as primary, secondary, or tertiary, depending on whether the –OH group is bonded to a primary, secondary, or tertiary carbon. For example, the compound 5-methyl-3-hexanol is a secondary alcohol.




**5-methyl-3-hexanol**



Ethers, especially those with two different alkyl groups (ROR′), can be prepared by a substitution reaction in which a nucleophilic alkoxide ion ($RO^-$) attacks the partially positively charged carbon atom of the polar C–X bond of an alkyl halide (R′X):



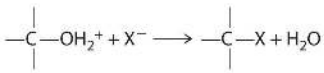

Although both alcohols and phenols have an –OH functional group, phenols are $10^6$–$10^8$ more acidic than alcohols. This is largely because simple alcohols have the –OH unit attached to an $sp^3$ hybridized carbon, whereas phenols have an $sp^2$ hybridized carbon atom bonded to the oxygen atom. The negative charge of the phenoxide ion can therefore interact with the π electrons in the ring, thereby delocalizing and stabilizing the negative charge through resonance. In contrast, the negative charge on an alkoxide ion cannot be stabilized by these types of interactions.

Alcohols undergo two major types of reactions: those involving cleavage of the O–H bond and those involving cleavage of the C–O bond. Cleavage of an O–H bond is a reaction characteristic of an acid, but alcohols are even weaker acids than water. The acidic strength of phenols, however, is about a million times greater than that of ethanol, making the $pK_a$ of phenol comparable to that of the $NH_4^+$ ion (9.89 versus 9.25, respectively):

$$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^- \tag{24.5.1}$$

> *Alcohols undergo two major types of reactions: cleavage of the O–H bond and cleavage of the C–O bond.*

Cleavage of the C–O bond in alcohols occurs under acidic conditions. The –OH is first protonated, and nucleophilic substitution follows:




In the absence of a nucleophile, however, elimination can occur, producing an alkene (Figure 24.5.6). Ethers lack the –OH unit that is central to the reactivity of alcohols, so they are comparatively unreactive. Their low reactivity makes them highly suitable as solvents for carrying out organic reactions.

## Aldehydes and Ketones

Aromatic aldehydes, which have intense and characteristic flavors and aromas, are the major components of such well-known flavorings as vanilla and cinnamon (Figure 24.5.3). Many ketones, such as camphor and jasmine, also have intense aromas. Ketones are found in many of the hormones responsible for sex differentiation in humans, such as progesterone and testosterone.

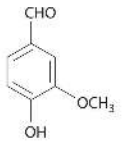
| Name | Formula | Use |
|---|---|---|
| Formaldehyde | $CH_2O$ | Biological preservative |
| Cinnamaldehyde | $C_6H_5CH{=}CHCHO$ | Cinnamon |
| Citral | $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCHO$ | Antiseptic, perfumes |
| Benzaldehyde | $C_6H_5CHO$ | Manufacture of dyes, almond flavoring |
| Vanillin |  | Vanilla flavoring |

Figure 23.6.3: Some Familiar Aldehydes and Their Uses

In compounds containing a carbonyl group, nucleophilic attack can occur at the carbon atom of the carbonyl, whereas electrophilic attack occurs at oxygen.




Aldehydes and ketones contain the carbonyl functional group, which has an appreciable dipole moment because of the polar C=O bond. The presence of the carbonyl group results in strong intermolecular interactions that cause aldehydes and ketones to have higher boiling points than alkanes or alkenes of comparable molecular mass (Table 24.5.3). As the mass of the molecule increases, the carbonyl group becomes less important to the overall properties of the compound, and the boiling points approach those of the corresponding alkanes.

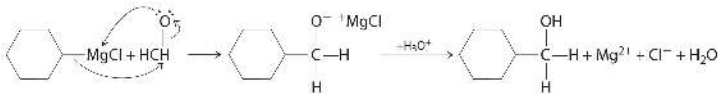
Table 23.6.2: Boiling Points of Alkanes, Aldehydes, and Ketones of Comparable Molecular Mass

| | Name | Formula | Molecular Mass (amu) | Boiling Point (°C) |
|---|---|---|---|---|
| alkane | n-butane | $C_4H_{10}$ | 58 | −0.5 |
| | n-pentane | $C_5H_{12}$ | 72 | 36.1 |
| aldehyde | propionaldehyde (propanal) | $C_3H_6O$ | 58 | 48.0 |
| | butyraldehyde (butanal) | $C_4H_8O$ | 72 | 74.8 |
| ketone | acetone (2-propanone) | $C_3H_6O$ | 58 | 56.1 |
| | methyl ethyl ketone (2-butanone) | $C_4H_8O$ | 72 | 79.6 |

Aldehydes and ketones are typically prepared by oxidizing alcohols (part (a) in Figure 24.5.7). In their reactions, the partially positively charged carbon atom of the carbonyl group is an electrophile that is subject to nucleophilic attack. Conversely, the lone pairs of electrons on the oxygen atom of the carbonyl group allow electrophilic attack to occur. Aldehydes and ketones can therefore undergo both nucleophilic attack (at the carbon atom) and electrophilic attack (at the oxygen atom).

> *Nucleophilic attack occurs at the partially positively charged carbon of a carbonyl functional group. Electrophilic attack occurs at the lone pairs of electrons on the oxygen atom.*

Aldehydes and ketones react with many organometallic compounds that contain stabilized carbanions. One of the most important classes of such compounds are the Grignard reagents, organomagnesium compounds with the formula RMgX (X is Cl, Br, or I) that are so strongly polarized that they can be viewed as containing $R^-$ and $MgX^+$. These reagents are named for the French chemist Victor Grignard (1871–1935), who won a Nobel Prize in Chemistry in 1912 for their development. In a Grignard reaction, the carbonyl functional group is converted to an alcohol, and the carbon chain of the carbonyl compound is lengthened by the addition of the R group from the Grignard reagent. One example is reacting cyclohexylmagnesium chloride, a Grignard reagent, with formaldehyde:

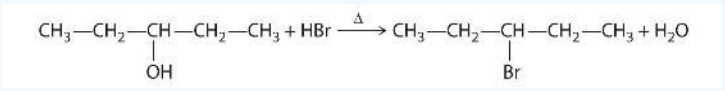



The nucleophilic carbanion of the cyclohexyl ring attacks the electrophilic carbon atom of the carbonyl group. Acidifying the solution results in protonation of the intermediate to give the alcohol. Aldehydes can also be prepared by reducing a carboxylic acid group ($–CO_2H$) (part (a) in Figure 24.5.7), and ketones can be prepared by reacting a carboxylic acid derivative with a Grignard reagent. The former reaction requires a powerful reducing agent, such as a metal hydride.

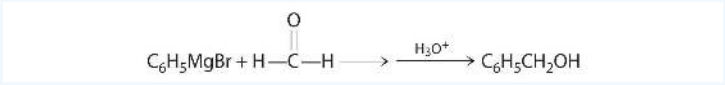
### ✔ 23.6.1

Explain how each reaction proceeds to form the indicated product.

a.




b.




**Given**: chemical reaction

**Asked for**: how products are formed

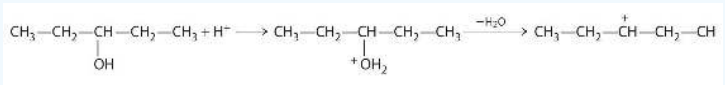
**Strategy:**

A. Identify the functional group and classify the reaction.
B. Use the mechanisms described to propose the initial steps in the reaction.

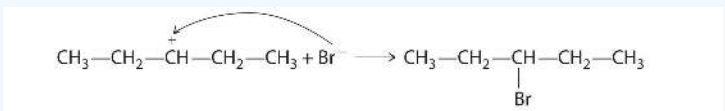
Solution:

a. A One reactant is an alcohol that undergoes a substitution reaction.

B In the product, a bromide group is substituted for a hydroxyl group. The first step in this reaction must therefore be protonation of the –OH group of the alcohol by $H^+$ of HBr, followed by the elimination of water to give the carbocation:

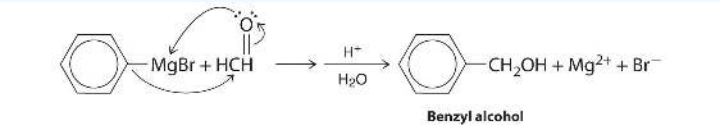



The bromide ion is a good nucleophile that can react with the carbocation to give an alkyl bromide:



b. A One reactant is a Grignard reagent, and the other contains a carbonyl functional group. Carbonyl compounds act as electrophiles, undergoing nucleophilic attack at the carbonyl carbon.

B The nucleophile is the phenyl carbanion of the Grignard reagent:



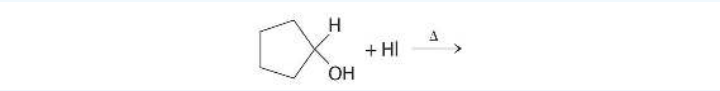

Benzyl alcohol

The product is benzyl alcohol.

## ? Exercise 23.6.1

Predict the product of each reaction.

a.




b.

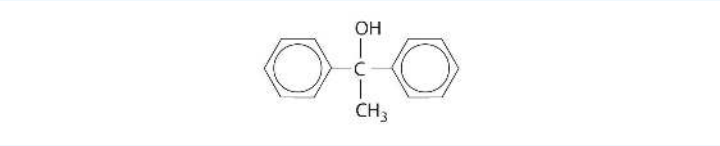



Answer:

a.



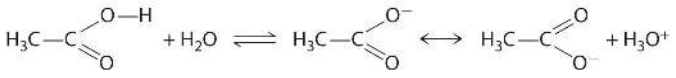

b.



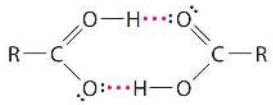

## Carboxylic Acids

The pungent odors of many carboxylic acids are responsible for the smells we associate with sources as diverse as Swiss cheese, rancid butter, manure, goats, and sour milk. The boiling points of carboxylic acids tend to be somewhat higher than would be expected from their molecular masses because of strong hydrogen-bonding interactions between molecules. In fact, most simple carboxylic acids form dimers in the liquid and even in the vapor phase. The four lightest carboxylic acids are completely miscible with water, but as the alkyl chain lengthens, they become more “alkane-like,” so their solubility in water decreases.

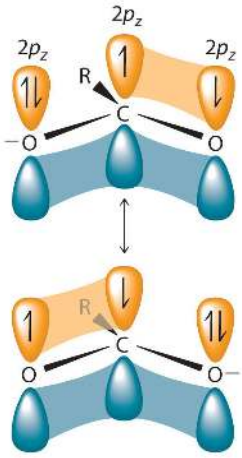
Compounds that contain the carboxyl functional group are acidic because carboxylic acids can easily lose a proton: the negative charge in the carboxylate ion ($RCO_2^-$) is stabilized by delocalization of the π electrons:




As a result, carboxylic acids are about $10^{10}$ times more acidic than the corresponding simple alcohols whose anions ($RO^-$) are not stabilized through resonance.



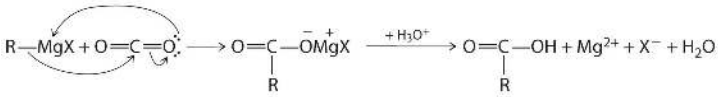
Hydrogen-bonded carboxylic acid molecules



Carboxylic acids are typically prepared by oxidizing the corresponding alcohols and aldehydes (part (a) in Figure 24.5.7). They can also be prepared by reacting a Grignard reagent with $CO_2$, followed by acidification:

$$CO_2 + RMgCl \xrightarrow{H_3O^+} RCO_2H + Mg^{2+} + Cl^- + H_2O \tag{24.5.2}$$

The initial step in the reaction is nucleophilic attack by the $R^-$ group of the Grignard reagent on the electrophilic carbon of $CO_2$:



Delocalization of π bonding over three atoms (O–C–O) makes carboxylic acids and their derivatives less susceptible to nucleophilic attack than aldehydes and ketones with their single π bond. The reactions of carboxylic acids are dominated by two factors: their polar $–CO_2H$ group and their acidity. Reaction with strong bases, for example, produce carboxylate salts, such as sodium stearate:

$$RCO_2H + NaOH \rightarrow RCO_2^- Na^+ + H_2O \tag{24.5.3}$$

where R is $CH_3(CH_2)_{16}$. As you learned in previously long-chain carboxylate salts are used as soaps.

> *Delocalization of π bonding over three atoms makes carboxylic acids and their derivatives less susceptible to nucleophilic attack as compared with aldehydes and ketones.*

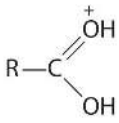
## Carboxylic Acid Derivatives

Replacing the –OH of a carboxylic acid with groups that have different tendencies to participate in resonance with the C=O functional group produces derivatives with rather different properties. Resonance structures have significant effects on the reactivity of carboxylic acid derivatives, but their influence varies substantially, being least important for halides and most important for the nitrogen of amides. In this section, we take a brief look at the chemistry of two of the most familiar and important carboxylic acid derivatives: esters and amides.

### Esters

Esters have the general formula $RCO_2R'$, where R and R′ can be virtually any alkyl or aryl group. Esters are often prepared by reacting an alcohol (R′OH) with a carboxylic acid ($RCO_2H$) in the presence of a catalytic amount of strong acid. The purpose of the

acid (an electrophile) is to protonate the doubly bonded oxygen atom of the carboxylic acid (a nucleophile) to give a species that is more electrophilic than the parent carboxylic acid.




**Protonated carboxylic acid**

The nucleophilic oxygen atom of the alcohol attacks the electrophilic carbon atom of the protonated carboxylic acid to form a new C–O bond. The overall reaction can be written as follows:

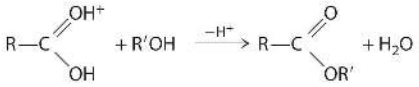
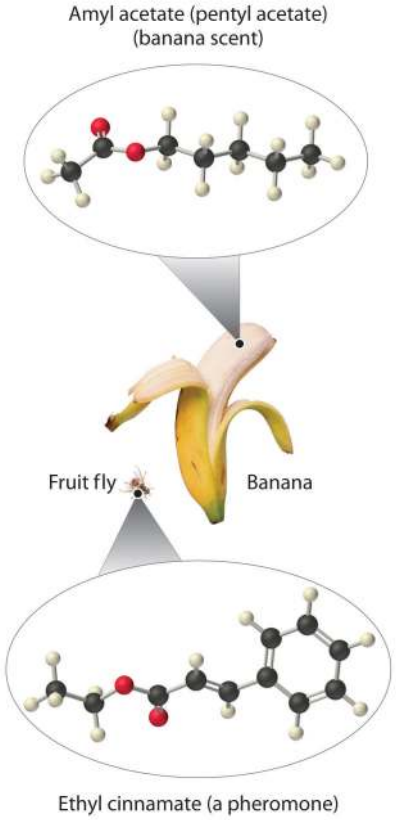



Figure 23.6.4

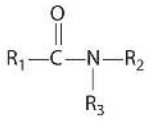
Because water is eliminated, this is a dehydration reaction. If an aqueous solution of an ester and strong acid or base is heated, the reverse reaction will occur, producing the parent alcohol R′OH and either the carboxylic acid $RCO_2H$ (under strongly acidic conditions) or the carboxylate anion $RCO_2^-$ (under basic conditions).

As stated earlier, esters are familiar to most of us as fragrances, such as banana and pineapple. Other esters with intense aromas function as sex attractants, or pheromones, such as the pheromone from the oriental fruit fly. Research on using synthetic insect pheromones as a safer alternative to insecticides for controlling insect populations, such as cockroaches, is a rapidly growing field in organic chemistry.



## Amides

In the general structure of an amide,



An amide

the two substituents on the amide nitrogen can be hydrogen atoms, alkyl groups, aryl groups, or any combination of those species. Although amides appear to be derived from an acid and an amine, in practice they usually cannot be prepared by this synthetic route. In principle, nucleophilic attack by the lone electron pair of the amine on the carbon of the carboxylic acid could occur, but because carboxylic acids are weak acids and amines are weak bases, an acid–base reaction generally occurs instead:

$$RCO_2H + R'NH_2 \rightarrow RCO_2^- + R'NH_3^+ \tag{24.5.4}$$

Amides are therefore usually prepared by the nucleophilic reaction of amines with more electrophilic carboxylic acid derivatives, such as esters.

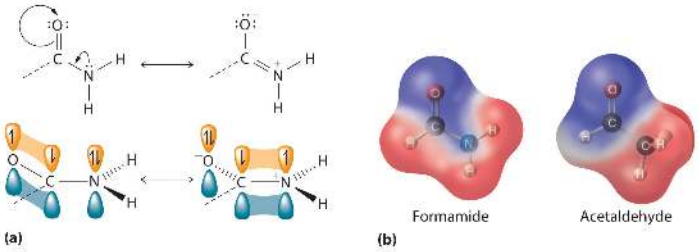
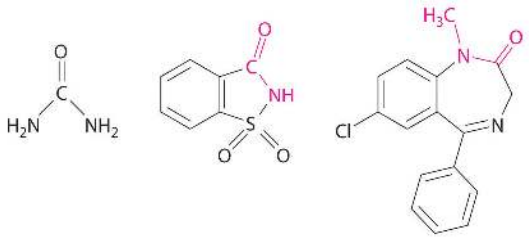



Figure 23.6.5: The Electronic Structure of an Amide. (a) An unhybridized 2pz orbital on nitrogen, containing a lone electron pair of electrons, can interact with the π orbital of the carbonyl group to give a three-center, four-electron bond. This interaction reduces the reactivity of the amide, making amides the least reactive of the carboxylic acid derivatives. (b) A comparison of the electrostatic potential maps of acetaldehyde and formamide shows that the negative charge (indicated in blue) is more localized on the oxygen atom of acetaldehyde than it is in formamide. Formamide is therefore less reactive.

The lone pair of electrons on the nitrogen atom of an amide can participate in π bonding with the carbonyl group, thus reducing the reactivity of the amide (Figure 24.5.5) and inhibiting free rotation about the C–N bond. Amides are therefore the least reactive of the carboxylic acid derivatives. The stability of the amide bond is crucially important in biology because amide bonds form the backbones of peptides and proteins. The amide bond is also found in many other biologically active and commercially important molecules, including penicillin; urea, which is used as fertilizer; saccharin, a sugar substitute; and valium, a potent tranquilizer.



Urea Saccharin Valium

> *Amides are the least reactive of the carboxylic acid derivatives because amides participate in π bonding with the carbonyl group.*

## Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. They are therefore analogous to alcohols and ethers. Like alcohols, amines are classified as primary, secondary, or tertiary, but in this case the designation refers to the number of alkyl groups bonded to the nitrogen atom, not to the number of adjacent carbon atoms. In primary amines, the nitrogen is bonded to two hydrogen atoms and one alkyl group; in secondary amines, the nitrogen is bonded to

one hydrogen and two alkyl groups; and in tertiary amines, the nitrogen is bonded to three alkyl groups. With one lone pair of electrons and C–N bonds that are less polar than C–O bonds, ammonia and simple amines have much lower boiling points than water or alcohols with similar molecular masses. Primary amines tend to have boiling points intermediate between those of the corresponding alcohol and alkane. Moreover, secondary and tertiary amines have lower boiling points than primary amines of comparable molecular mass.

Tertiary amines form cations analogous to the ammonium ion ($NH_4^+$), in which all four H atoms are replaced by alkyl groups. Such substances, called quaternary ammonium salts, can be chiral if all four substituents are different. (Amines with three different substituents are also chiral because the lone pair of electrons represents a fourth substituent.)

Alkylamines can be prepared by nucleophilic substitution reactions of alkyl halides with ammonia or other amines:

$$RCl + NH_3 \rightarrow RNH_2 + HCl \tag{24.5.5}$$

$$RCl + R'NH_2 \rightarrow RR'NH + HCl \tag{24.5.6}$$

$$RCl + R'R''NH \rightarrow RR'R''N + HCl \tag{24.5.7}$$

The primary amine formed in the first reaction (Equation 24.5.5) can react with more alkyl halide to generate a secondary amine (Equation 24.5.6), which in turn can react to form a tertiary amine (Equation 24.5.7). Consequently, the actual reaction mixture contains primary, secondary, and tertiary amines and even quaternary ammonium salts.

The reactions of amines are dominated by two properties: their ability to act as weak bases and their tendency to act as nucleophiles, both of which are due to the presence of the lone pair of electrons on the nitrogen atom. Amines typically behave as bases by accepting a proton from an acid to form an ammonium salt, as in the reaction of triethylamine (the ethyl group is represented as Et) with aqueous HCl (the lone pair of electrons on nitrogen is shown):

$$Et_3N : (l) + HCl(aq) \rightarrow Et_3NH^+Cl^-_{(aq)} \backslash tag 24.5.8 \tag{23.6.1}$$

which gives triethylammonium chloride. Amines can react with virtually any electrophile, including the carbonyl carbon of an aldehyde, a ketone, or an ester. Aryl amines such as aniline ($C_6H_5NH_2$) are much weaker bases than alkylamines because the lone pair of electrons on nitrogen interacts with the π bonds of the aromatic ring, delocalizing the lone pair through resonance (Figure 24.5.6).

**Note**

The reactions of amines are dominated by their ability to act as weak bases and their tendency to act as nucleophiles.

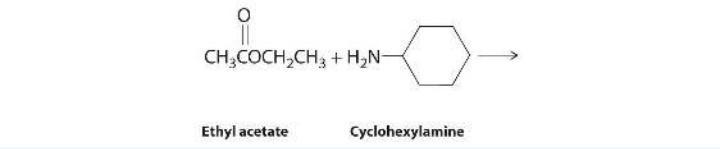
Figure 23.6.6: Structures and Basicity of Aniline and Cyclohexylamine

Delocalization of the lone electron pair on N over the benzene ring reduces the basicity of aryl amines, such as aniline, compared with that of alkylamines, such as cyclohexylamine. These electrostatic potential maps show that the electron density on the N of cyclohexylamine is more localized than it is in aniline, which makes cyclohexylamine a stronger base.

**Example 23.6.2**

Predict the products formed in each reaction and show the initial site of attack and, for part (b), the final products.

a. $C_6H_5CH_2CO_2H$ + KOH →
b.




**Given**: reactants

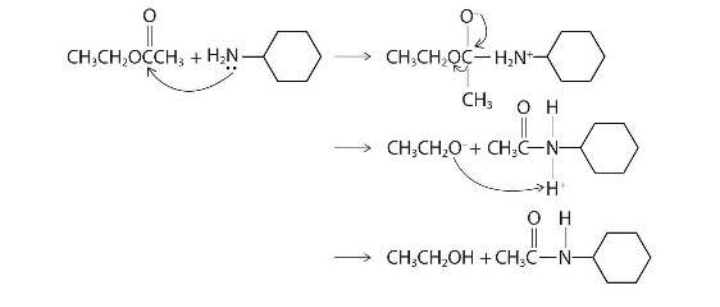
**Asked for**: products and mechanism of reaction

**Strategy**:

Use the strategy outlined in Example 7.

**Solution**:

a. The proton on the carboxylic acid functional group is acidic. Thus reacting a carboxylic acid with a strong base is an acid–base reaction, whose products are a salt—in this case, $C_6H_5CH_2CO_2^-K^+$—and water.
b. The nitrogen of cyclohexylamine contains a lone pair of electrons, making it an excellent nucleophile, whereas the carbonyl carbon of ethyl acetate is a good electrophile. We therefore expect a reaction in which nucleophilic attack on the carbonyl carbon of the ester produces an amide and ethanol. The initial site of attack and the reaction products are as follows:



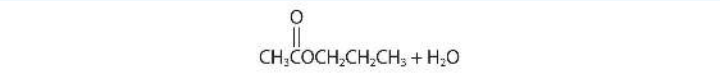
## Exercise 23.6.2

Predict the products of each reaction. State the initial site of attack.

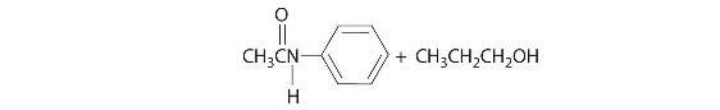
a. acetic acid with 1-propanol
b. aniline ($C_6H_5NH_2$) with propyl acetate [$CH_3C(=O)OCH_2CH_2CH_3$]

**Answer**:

a. Initial attack occurs with protonation of the oxygen of the carbonyl. The products are:



b. Initial attack occurs at the carbon of the carbonyl group. The products are:



Reactions like we have discussed in this section are used to synthesize a wide range of organic compounds. When chemists plan the synthesis of an organic molecule, however, they must take into consideration various factors, such as the availability and cost of reactants, the need to minimize the formation of undesired products, and the proper sequencing of reactions to maximize the yield of the target molecule and minimize the formation of undesired products. Because the synthesis of many organic molecules requires multiple steps, in designing a synthetic scheme for such molecules, chemists must often work backward from the desired product in a process called retrosynthesis. Using this process, they can identify the reaction steps needed to synthesize the desired product from the available reactants.

## Summary

- The physical properties and reactivity of compounds containing the common functional groups are intimately connected to their structures.

There are strong connections among the structure, the physical properties, and the reactivity for compounds that contain the major functional groups. Hydrocarbons that are alkanes undergo catalytic cracking, which can convert straight-chain alkanes to highly branched alkanes. Catalytic cracking is one example of a pyrolysis reaction, in which the weakest bond is cleaved at high temperature, producing a mixture of radicals. The multiple bond of an alkene produces geometric isomers (cis and trans). Terminal alkynes contain a hydrogen atom directly attached to a triply bonded carbon. Removal of the hydrogen forms an acetylide ion, a potent nucleophile used to make longer carbon chains. Arenes undergo substitution rather than elimination because of enhanced stability from delocalization of their π electron density. An alcohol is often prepared by adding the elements of water across a double bond or by a substitution reaction. Alcohols undergo two major types of reactions: those involving cleavage of the O–H bond and those involving cleavage of the C–O bond. Phenols are acidic because of π interactions between the oxygen atom and the ring. Ethers are comparatively unreactive. Aldehydes and ketones are generally prepared by oxidizing alcohols. Their chemistry is characterized by nucleophilic attack at the carbon atom of the carbonyl functional group and electrophilic attack at the oxygen atom. Grignard reagents (RMgX, where X is Cl, Br, or I) convert the carbonyl functional group to an alcohol and lengthen the carbon chain. Compounds that contain the carboxyl functional group are weakly acidic because of delocalization of the π electrons, which causes them to easily lose a proton and form the carboxylate anion. Carboxylic acids are generally prepared by oxidizing alcohols and aldehydes or reacting a Grignard reagent with $CO_2$. Carboxylic acid derivatives include esters, prepared by reacting a carboxylic acid and an alcohol, and amides, prepared by the nucleophilic reaction of amines with more electrophilic carboxylic acid derivatives, such as esters. Amides are relatively unreactive because of π bonding interactions between the lone pair on nitrogen and the carbonyl group. Amines can also be primary, secondary, or tertiary, depending on the number of alkyl groups bonded to the amine. Quaternary ammonium salts have four substituents attached to nitrogen and can be chiral. Amines are often prepared by a nucleophilic substitution reaction between a polar alkyl halide and ammonia or other amines. They are nucleophiles, but their base strength depends on their substituents.

## Conceptual Problems

1. Why do branched-chain alkanes have lower melting points than straight-chain alkanes of comparable molecular mass?
2. Describe alkanes in terms of their orbital hybridization, polarity, and reactivity. What is the geometry about each carbon of a straight-chain alkane?
3. Why do alkenes form cis and trans isomers, whereas alkanes do not? Do alkynes form cis and trans isomers? Why or why not?
4. Which compounds can exist as cis and trans isomers?

    a. 2,3-dimethyl-1-butene
    b. 3-methyl-1-butene
    c. 2-methyl-2-pentene
    d. 2-pentene

5. Which compounds can exist as cis and trans isomers?

    a. 3-ethyl-3-hexene
    b. 1,1-dichloro-1-propene
    c. 1-chloro-2-pentene
    d. 3-octene

6. Which compounds have a net dipole moment?

    a. o-nitrotoluene
    b. p-bromonitrobenzene
    c. p-dibromobenzene

7. Why is the boiling point of an alcohol so much greater than that of an alkane of comparable molecular mass? Why are low-molecular-mass alcohols reasonably good solvents for some ionic compounds, whereas alkanes are not?

8. Is an alcohol a nucleophile or an electrophile? What determines the mode of reactivity of an alcohol? How does the reactivity of an alcohol differ from that of an ionic compound containing OH, such as KOH?
9. How does the reactivity of ethers compare with that of alcohols? Why? Ethers can be cleaved under strongly acidic conditions. Explain how this can occur.
10. What functional group is common to aldehydes, ketones, carboxylic acids, and esters? This functional group can react with both nucleophiles and electrophiles. Where does nucleophilic attack on this functional group occur? Where does electrophilic attack occur?
11. What key feature of a Grignard reagent allows it to engage in a nucleophilic attack on a carbonyl carbon?
12. Do you expect carboxylic acids to be more or less water soluble than ketones of comparable molecular mass? Why?
13. Because amides are formally derived from an acid plus an amine, why can they not be prepared by the reaction of an acid with an amine? How are they generally prepared?
14. Is an amide susceptible to nucleophilic attack, electrophilic attack, or both? Specify where the attack occurs.
15. What factors determine the reactivity of amines?

## Answers

5. (c) and (d)

11. The presence of a nucleophilic $C^{\delta-}$ resulting from a highly polar interaction with an electropositive Mg

15. Their ability to act as weak bases and their tendency to act as nucleophiles

## Structure and Reactivity

1. What is the product of the reaction of 2-butyne with excess HBr?
2. What is the product of the reaction of 3-hexyne with excess HCl?
3. What elements are eliminated during the dehydrohalogenation of an alkyl halide? What products do you expect from the dehydrohalogenation of 2-chloro-1-pentene?
4. What elements are eliminated during the dehydration of an alcohol? What products do you expect from the dehydration of ethanol?
5. Predict the products of each reaction.
    a. sodium phenoxide with ethyl chloride
    b. 1-chloropropane with NaOH
6. Show the mechanism and predict the organic product of each reaction.
    a. 2-propanol + HCl
    b. cyclohexanol + $H_2SO_4$
7. A Grignard reagent can be used to generate a carboxylic acid. Show the mechanism for the first step in this reaction using $CH_3CH_2MgBr$ as the Grignard reagent. What is the geometry about the carbon of the $–CH_2$ of the intermediate species formed in this first step?
8. Draw a molecular orbital picture showing the bonding in an amide. What orbital is used for the lone pair of electrons on nitrogen?
9. What is the product of the reaction of
    a. acetic acid with ammonia?
    b. methyl acetate with ethylamine, followed by heat?
10. Develop a synthetic scheme to generate
    a. 1,1-dichloroethane from 1,1-dibromoethane.
    b. 2-bromo-1-heptene from 1-bromopentane.

## Answers

1. 2,2-dibromobutane

5.

a. $C_6H_5OC_2H_5$ + NaCl
b. 1-propanol + NaCl

9.

a. $CH_3CO_2^-$ $NH_4^+$ (an acid-base reaction)
b. $CH_3CONHC_2H_5$ + $CH_3OH$

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# 23.7: The Molecules of Life

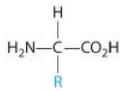
**Learning Objectives**

- To identify the common structural units of important biological molecules.

All the functional groups described in this chapter are found in the organic molecules that are constantly synthesized and destroyed by every living organism on Earth. A detailed understanding of the reactions that occur in living organisms is the goal of biochemistry, which deals with a wide variety of organic structures and reactions. The most abundant substances found in living systems belong to four major classes: proteins, carbohydrates, lipids, and nucleic acids. Here we briefly describe the structure and some functions of these biological molecules.

## Proteins

In Section 12.8, we described proteinsA biological polymer with more than 50 amino acid residues linked together by amide bonds. as biologically active polymers formed from amino acids linked together by amide bonds. In addition to an amine group and a carboxylic acid group, each amino acid contains a characteristic R group (Figure 9.7.1). In the simplest amino acid, glycine, the R group is hydrogen (–H), but in other naturally occurring amino acids, the R group may be an alkyl group or a substituted alkyl group, a carboxylic group, or an aryl group. The nature of the R group determines the particular chemical properties of each amino acid. In Figure 9.7.1, all the amino acids found in proteins except glycine are chiral compounds, which suggests that their interactions with other chiral compounds are selective. Some proteins, called enzymes, catalyze biological reactions, whereas many others have structural, contractile, or signaling functions. Because we have described proteins previously, we will not discuss them further.




**The general structure of an amino acid.** An amino acid is chiral except when R is an H atom.

## Carbohydrates

*Carbohydrates* are the most abundant of the organic compounds found in nature. They constitute a substantial portion of the food we consume and provide us with the energy needed to support life. Table sugar, milk, honey, and fruits all contain low-molecular-mass carbohydrates that are easily assimilated by the human body. In contrast, the walls of plant cells and wood contain high-molecular-mass carbohydrates that we cannot digest.

Once thought to be hydrates of carbon with the general formula $C_n(H_2O)_m$, carbohydrates are actually polyhydroxy aldehydes or polyhydroxy ketones (i.e., aldehydes or ketones with several –OH groups attached to the parent hydrocarbon). The simplest carbohydrates consist of unbranched chains of three to eight carbon atoms: one carbon atom is part of a carbonyl group, and some or all of the others are bonded to hydroxyl groups. The structure of a carbohydrate can be drawn either as a hydrocarbon chain, using a *Fischer projection*, or as a ring, using a *Haworth projection* (Figure 23.6.1). The Haworth projection is named after the British chemist Sir Walter Norman Haworth, who was awarded a Nobel Prize in Chemistry in 1937 for his discovery that sugars exist mainly in their cyclic forms, as well as for his collaboration on the synthesis of vitamin C. The cyclic form is the product of nucleophilic attack by the oxygen of a hydroxyl group on the electrophilic carbon of the carbonyl group within the same molecule, producing a stable ring structure composed of five or six carbons that minimizes bond strain (Figure 23.6.1). The substituents on the right side of the carbon chain in a Fischer projection are in the “down” position in the corresponding Haworth projection. Attack by the hydroxyl group on either side of the carbonyl group leads to the formation of two cyclic forms, called *anomers*: an α form, with the –OH in the “down” position, and a β form, with the –OH in the “up” position.

### Walter Norman Haworth (1883–1950)

At age 14, Walter Norman Haworth left school to join his father to learn linoleum design and manufacturing, but he became interested in chemistry through his use of dyes. Private tutoring enabled him to pass the entrance exam of the University of

Manchester, where he received his doctorate in 1911. During World War I, Haworth organized the laboratories at St. Andrews for the production of chemicals and drugs, returning to the investigation of carbohydrates after the war.

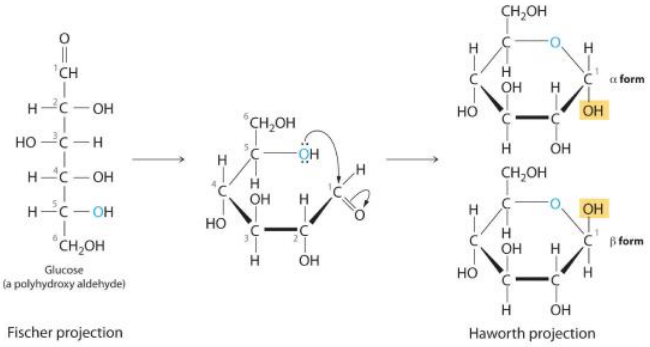
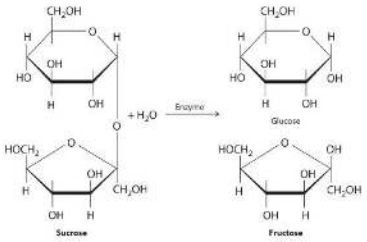


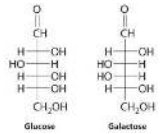

Figure 23.6.1 Fischer Projection and Haworth Projection of **Glucose** In solution, simple sugars exist predominantly in the ring form, the product of nucleophilic attack by the oxygen of a hydroxyl group on the electrophilic carbon of the carbonyl group. The α and β forms, called anomers, differ in the configuration at C1.

Carbohydrates are classified according to the number of single *saccharide*, or sugar, units they contain (from the Latin *saccharum*, meaning "sugar"). The simplest are *monosaccharides*; a *disaccharide* consists of two linked monosaccharide units; a *trisaccharide* has three linked monosaccharide units; and so forth. Glucose is a monosaccharide, and sucrose (common table sugar) is a disaccharide. The hydrolysis of sucrose produces glucose and another monosaccharide, fructose, in a reaction catalyzed by an enzyme or by acid:

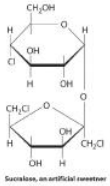



*Polysaccharides* hydrolyze to produce more than 10 monosaccharide units.

The common monosaccharides contain several chiral carbons and exist in several isomeric forms. One isomer of glucose, for example, is galactose, which differs from glucose in the position of the –OH bond at carbon-4:




Because carbons-2, -3, -4, and -5 of glucose are chiral, changing the position of the –OH on carbon-4 does not produce an enantiomer of glucose but a different compound, galactose, with distinct physical and chemical properties. Galactose is a hydrolysis product of lactose, a disaccharide found in milk. People who suffer from *galactosemia* lack the enzyme needed to convert galactose to glucose, which is then metabolized to $CO_2$ and $H_2O$, releasing energy. Galactose accumulates in their blood and tissues, leading to mental retardation, cataracts, and cirrhosis of the liver.



Because carbohydrates have a carbonyl functional group and several hydroxyl groups, they can undergo a variety of biochemically important reactions. The carbonyl group, for example, can be oxidized to form a carboxylic acid or reduced to form an alcohol. The

hydroxyl groups can undergo substitution reactions, resulting in derivatives of the original compound. One such derivative is Sucralose, an artificial sweetener that is six times sweeter than sucrose; it is made by replacing two of the hydroxyl groups on sucrose with chlorine. Carbohydrates can also eliminate hydroxyl groups, producing alkenes.

### Note the Pattern

Because carbohydrates have a carbonyl functional group and several hydroxyl groups, they can undergo a variety of reactions.

Two familiar polysaccharides are *starch* and *cellulose*, which both hydrolyze to produce thousands of glucose units. They differ only in the connection between glucose units and the amount of branching in the molecule (Figure 23.6.2). Starches can be coiled or branched and are hydrolyzed by the enzymes in our saliva and pancreatic juices. Animal starch, called *glycogen*, is stored in the liver and muscles. It consists of branched glucose units linked by bonds that produce a coiled structure. The glucose units in cellulose, in contrast, are linked to give long, unbranched chains. The chains in cellulose stack in parallel rows held together by hydrogen bonds between hydroxyl groups. This arrangement produces a rigid structure that is insoluble in water.

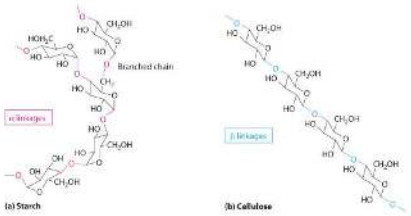
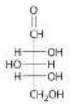



Figure 23.6.2 The Polysaccharides Starch and **Cellulose** Starches (a) and cellulose (b) differ in the connection between glucose units and the amount of branching in the molecule. Starches can be coiled or branched, whereas cellulose, the primary structural material of plants, has long, unbranched chains held together by hydrogen bonds.

Cellulose is the primary structural material of plants and one of the most abundant organic substances on Earth. Because our enzymes are not able to hydrolyze the bonds between the glucose units in cellulose, we are unable to digest it. A recently marketed product containing a high percentage of cellulose was sold as a dietetic substance for rapid weight loss, but those who consumed it experienced severe intestinal discomfort because the cellulose could not be digested. The product was quickly removed from the market.

### Example 23.6.1

The Fischer projection of xylose, found in many varieties of apples, is shown. Draw the ring form (Haworth projection) of xylose.



**Given:** Fischer projection of a sugar

**Asked for:** cyclic structure

**Strategy:**

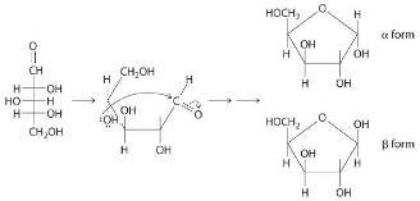
**A** Identify the nucleophile and the electrophile. Indicate the point of attack, remembering that cyclic structures are most stable when they contain at least five atoms in the ring to prevent bond strain from bond angles that are too small.

**B** Draw the cyclic form of the structure.

**Solution:**

**A** The carbonyl carbon (C1) is a good electrophile, and each oxygen is a good nucleophile. Nucleophilic attack occurs from the –OH group on C4, producing a stable five-membered ring.

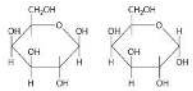
**B** Because of rotation about the bond between C1 and C2, ring formation gives both a and b anomers, with the following structures (H atoms have been omitted for clarity):



Exercise

Draw the cyclic form(s) of galactose, whose Fischer projection is shown in the previous discussion.

**Answer**



## Lipids

LipidsA family of compounds that includes fats, waxes, some vitamins, and steroids and characterized by their insolubility in water. (from the Greek *lipos*, meaning “fat” or “lard”) are characterized by their insolubility in water. They form a family of compounds that includes fats, waxes, some vitamins, and steroids. *Fatty acids*, the simplest lipids, have a long hydrocarbon chain that ends with a carboxylic acid functional group. In saturated fatty acids, the hydrocarbon chains contain only C–C bonds, so they can stack in a regular array (part (a) in Figure 23.6.3). In contrast, unsaturated fatty acids have a single double bond in the hydrocarbon chain (monounsaturated) or more than one double bond (polyunsaturated). These double bonds give fatty acid chains a kinked structure, which prevents the molecules from packing tightly (part (b) in Figure 23.6.3). As a result of reduced van der Waals interactions, the melting point of an unsaturated fatty acid is lower than that of a saturated fatty acid of comparable molecule mass, thus producing an oil rather than a solid. (For more information on van der Waals interactions, see Section 11.2.) Fish oils and vegetable oils, for example, have a higher concentration of unsaturated fatty acids than does butter.

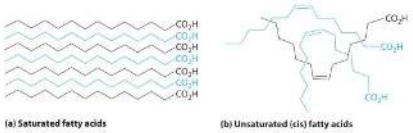



Figure 23.6.3 Fatty Acids, the Simplest Class of **Lipids**Fatty acids are composed of a long chain that terminates in a carboxylic acid functional group. (a) Molecules of saturated fatty acids, which contain no carbon–carbon double bonds, can stack in a regular array. (b) Molecules of unsaturated fatty acids, which contain one or more *cis* carbon–carbon double bonds, have kinked structures that cannot pack closely together.

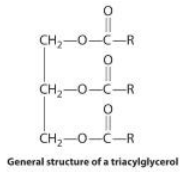
The double bonds of unsaturated fatty acids can by hydrogenated in an addition reaction that produces a saturated fatty acid:

$$\underset{unsaturated\ fatty\ acid}{-CH=CH-} + H_2 \rightarrow \underset{saturated\ fatty\ acid}{-CH_2CH_2-}$$

They can also be oxidized to produce an aldehyde or carboxylic acid. (For more information on hydrogenation, see Section 14.8.)

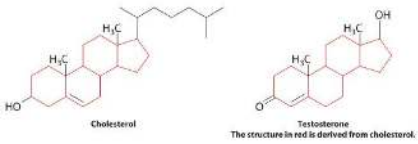
Unsaturated fatty acids are the starting compounds for the biosynthesis of *prostaglandins*. These hormone-like substances are involved in regulating blood pressure, tissue inflammation, and contracting and relaxing smooth muscles. Drugs such as aspirin and ibuprofen inhibit the production of prostaglandins, thereby reducing inflammation.

*Waxes* are esters produced by the nucleophilic attack of an alcohol on the carbonyl carbon of a long-chain carboxylic acid (Figure 23.5.4). For example, the wax used in shoe polish and wax paper, which is derived from beeswax, is formed from a straight-chain alcohol with 15 carbon atoms and a fatty acid with 31 carbon atoms. *Triacylglycerols* are a particularly important type of ester in living systems; they are used by the body to store fats and oils. These compounds are formed from one molecule of glycerol (1,2,3-trihydroxypropane) and three fatty acid molecules. During warmer months of the year, animals that hibernate consume large quantities of plants, seeds, and nuts that have a high fat and oil content. They convert the fatty acids to triacylglycerols and store them. Hydrolysis of stored triacylglycerols during hibernation (the reverse of Figure 23.5.4) releases alcohols and carboxylic acids that the animal uses to generate energy for maintaining cellular activity, respiration, and heart rate. Derivatives of triacylglycerols with a phosphate group are major components of all cell membranes.



General structure of a triacylglycerol

*Steroids* are lipids whose structure is composed of three cyclohexane rings and one cyclopentane ring fused together. The presence of various substituents, including double bonds, on the basic steroid ring structure produces a large family of steroid compounds with different biological activities. For example, *cholesterol*, a steroid found in cellular membranes, contains a double bond in one ring and four substituents: a hydroxyl group, two methyl groups, and a hydrocarbon chain.




Cholesterol is the starting point for the biosynthesis of steroid hormones, including testosterone, the primary male sex hormone, and progesterone, which helps maintain pregnancy. These cholesterol derivatives lack the long hydrocarbon side chain, and most contain one or more ketone groups.

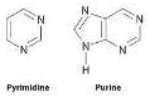
Cholesterol is synthesized in the human body in a multistep pathway that begins with a derivative of acetic acid. We also consume cholesterol in our diets: eggs, meats, fish, and diary products all contain cholesterol, but vegetables and other plant-derived foods do not contain cholesterol. Excess cholesterol in the human body can cause gallstones, which are composed of nearly 100% cholesterol, or lipid deposits called plaque in arteries. A buildup of plaque can block a coronary artery and result in a heart attack (Figure 23.6.4).




**Figure 23.6.4 Plaque in an Artery** Plaque, a lipid deposit, forms from excess cholesterol in the body. This artery is nearly blocked by a thick deposit of plaque, which greatly increases the risk of a heart attack due to reduced blood flow to the heart.

## Nucleic Acids

Nucleic acidsA linear polymer of nucleotides that is the basic structural component of DNA and RNA. are the basic structural components of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid), the biochemical substances found in the nuclei of all cells that transmit the information needed to direct cellular growth and reproduction. Their structures are derived from cyclic nitrogen-containing compounds called *pyrimidines* and *purines*, which can engage in hydrogen bonding through the lone electron pair on nitrogen (in pyrimidine and purine) or through the hydrogen of the amine (in purine):




The same cyclic structures are found in substances such as caffeine, a purine that is a stimulant, and the antifungal agent flucytosine, a pyrimidine. (For more information on the structure of caffeine, see Section 7.2.)

When a pyrimidine or a purine is linked to a sugar by a bond called a *glycosidic bond*, a *nucleoside* is formed. Adding a phosphoric acid group to the sugar then produces a *nucleotide* (part (a) in Figure 23.6.5). The linkage of nucleotides forms a polymeric chain that consists of alternating sugar and phosphate groups, which is the backbone of DNA and RNA (part (b) in Figure 23.6.5).

While the function of DNA is to preserve genetic information, RNA translates the genetic information in DNA and carries that information to cellular sites where proteins are synthesized. Many antibiotics function by interfering with the synthesis of proteins

in one or more kinds of bacteria. Chloramphenicol, for example, is used against infections of the eye or outer ear canal; it inhibits the formation of peptide bonds between amino acids in a protein chain. Puromycin, which is used against herpes simplex type I, interrupts extension of a peptide chain, causing the release of an incomplete protein and the subsequent death of the virus.

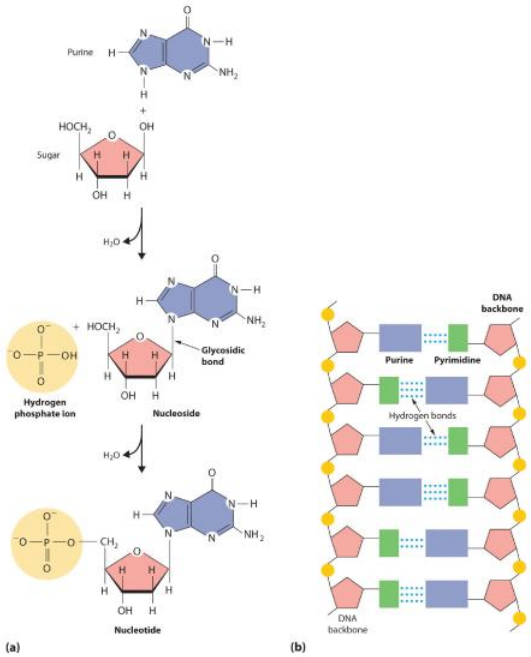



Figure 23.6.5 The Formation of Nucleic Acids(a) When pyrimidine or purine and a sugar react to form a glycosidic bond, a nucleoside is produced. Adding a phosphoric acid group to the sugar of a nucleoside produces a nucleotide. (b) Nucleotides link together to form long polymeric chains. A DNA molecule consists of two such chains held together by hydrogen bonding between the purine and pyrimidine components on different chains.

Mutations in the DNA of an organism may lead to the synthesis of defective proteins. *Phenylketonuria* (*PKU*), for example, is a condition caused by a defective enzyme. Left untreated, it produces severe brain damage and mental retardation. *Albinism* is caused by a defective enzyme that is unable to produce melanin, the pigment responsible for the color of skin and hair. *Cystic fibrosis*, the most common inherited disease in the United States, blocks pancreatic function and causes thick mucus secretions that make breathing difficult. An area of intense research in combating cancer involves the synthesis of drugs that stop uncontrolled cell growth by interfering with DNA replication.

## Key Takeaway

The four major classes of organic compounds found in biology are proteins, carbohydrates, lipids, and nucleic acids. Their structures and reactivity are determined by the functional groups present.

## Summary

**Proteins** are biologically active polymers formed from amino acids linked together by amide bonds. All the amino acids in proteins are chiral compounds except glycine. The most common organic compounds found in nature are the **carbohydrates**, polyhydroxy aldehydes or polyhydroxy ketones in unbranched chains of three to eight carbons. They are classified according to the number of sugar, or saccharide, units, and they can be drawn as a chain in a Fischer projection or in a cyclic form called a Haworth projection. The two cyclic forms in a Haworth projection are called anomers. Many sugars contain at least one chiral center. With their carbonyl and hydroxyl functional groups, carbohydrates can undergo a variety of biochemically relevant reactions. Starch and cellulose differ only in the connectivity between glucose units. Starches can be branched or unbranched, but cellulose, the structural material of plants, is unbranched, and cannot be digested by humans. **Lipids** are insoluble in water. The simplest lipids, fatty acids, have a long hydrocarbon chain ending in a carboxylic acid functional group. Their physical properties depend on the number of double bonds in the chain. Prostaglandins, hormone-like substances, are formed from unsaturated fatty acids, and waxes are long-chain esters of saturated fatty acids. Triacylglycerols, which the body uses to store fats and oils, consist of glycerol esterified to three fatty acid molecules. Steroids, which include cholesterol and the steroid hormones, are characterized by three cyclohexane rings and one cyclopentane ring fused together. The basic structural units of DNA and RNA are the **nucleic acids**,

whose structures are derived from nitrogen-containing cyclic compounds called pyrimidines and purines. These structures are linked to a sugar through a glycosidic bond, forming a nucleoside. Adding a phosphoric acid group produces a nucleotide. Nucleotides link to form a polymeric chain that is the backbone of DNA and RNA.

### Key Takeaway

- An understanding of the reactivity of functional groups is necessary to understanding the reactions that occur in living systems.

### Conceptual Problems

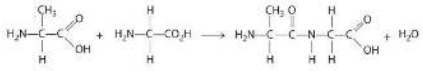
1. What are the strengths and limitations of using a Haworth projection? of using a Fischer projection?
2. Nutritionists will often state that a leafy salad contains no calories. Do you agree?
3. Would you expect margarine, a polyunsaturated fat, to have a higher or lower melting point than butter, a saturated fat?

### Structure and Reactivity

1. Propose a method for synthesizing the dipeptide alanylglycine (Ala-Gly), starting with the individual amino acids (Figure 9.7.1).
2. Are all the naturally occurring amino acids chiral compounds? Do you expect proteins to contain both enantiomers of alanine and other amino acids? Explain your answer.
3. The structures of cholesterol and testosterone were shown in this section. Identify the functional groups in each.
4. The structures of glucose and purine were shown in this section. Identify the functional groups in each.

### Answer

1. Use a condensation reaction:



2.
3.
4.

### Contributors

- Anonymous

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# CHAPTER OVERVIEW

## 24: Nuclear Chemistry

Until now, you have studied chemical processes in which atoms share or transfer electrons to form new compounds, leaving the atomic nuclei largely unaffected. In this chapter, we examine some properties of the atomic nucleus and the changes that can occur in atomic nuclei. Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, the identities of the elements change. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a *billion* times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

We begin by examining the structure of the atomic nucleus and the factors that determine whether a particular nucleus is stable or decays spontaneously to another element. We then discuss the major kinds of nuclear decay reactions, as well as the properties and uses of the radiation emitted when nuclei decay. You will learn how radioactive emissions can be used to study the mechanisms of chemical reactions and biological processes and how to calculate the amount of energy released during a nuclear reaction. You will also discover why houses are tested for radon gas, how radiation is used to probe organs such as the brain, and how the energy from nuclear reactions can be harnessed to produce electricity. Last, we explore the nuclear chemistry that takes place in stars, and we describe the role that stars play in producing most of the elements in the universe.


24.1: Introduction
24.2: The Components of the Nucleus
24.3: Nuclear Reactions
24.4: The Interaction of Nuclear Radiation with Matter
24.5: Thermodynamic Stability of the Atomic Nucleus
24.6: Applied Nuclear Chemistry
24.7: The Origin of the Elements
24.E: Nuclear Chemistry (Exercises)

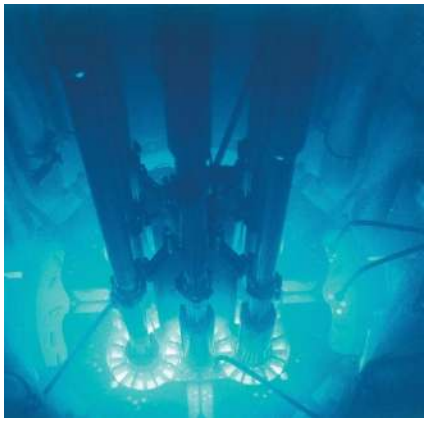

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# 24.1: Introduction

Until now, you have studied chemical processes in which atoms share or transfer electrons to form new compounds, leaving the atomic nuclei largely unaffected. In this chapter, we examine some properties of the atomic nucleus and the changes that can occur in atomic nuclei.

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We begin by examining the structure of the atomic nucleus and the factors that determine whether a particular nucleus is stable or decays spontaneously to another element. We then discuss the major kinds of nuclear decay reactions, as well as the properties and uses of the radiation emitted when nuclei decay. You will learn how radioactive emissions can be used to study the mechanisms of chemical reactions and biological processes and how to calculate the amount of energy released during a nuclear reaction. You will also discover why houses are tested for radon gas, how radiation is used to probe organs such as the brain, and how the energy from nuclear reactions can be harnessed to produce electricity. Last, we explore the nuclear chemistry that takes place in stars, and we describe the role that stars play in producing most of the elements in the universe.



**The glow caused by intense radiation.** The high-energy particles ejected into the surrounding water or air by an intense radioactive source such as this nuclear reactor core produce a ghostly bluish glow.

## Contributors

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# 24.2: The Components of the Nucleus

**Learning Objectives**

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or *decay*, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

## The Atomic Nucleus

As you learned in Chapter 1, each element can be represented by the notation <math display="inline" xml:id="av_1.0-20_m001" xmlns:xlink="http://www.w3.org/1999/xlink"><semantics><mrow><mmultiscripts/></mrow></semantics></math> <mtext>X</mtext><mprescripts/><mi>Z</mi><mi>A</mi><mtext>,</mtext> where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called nucleonsThe protons and neutrons that make up the nucleus of an atom., and an atom with a particular number of protons and neutrons is called a nuclideAn atom with a particular number of nucleons.. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

$$\begin{array}{cccc} {}^{A}_{Z}X: & {}^{16}_{8}O & {}^{17}_{8}O & {}^{18}_{8}O \\ {}^{A}X: & {}^{16}O & {}^{17}O & {}^{18}O \\ element-A & oxygen-16 & oxygen-17 & oxygen-18 \end{array}$$

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17.

Any nucleus that is unstable and decays spontaneously is said to be radioactiveAny nucleus that is unstable and decays spontaneously, emitting particles and electromagnetic radiation., emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called radioisotopesAn isotope that emits radiation. As you learned in Chapter 14, the rate at which radioactive decay occurs is characteristic of the isotope and is generally reported as a **half-life** ($t_{1/2}$), the amount of time required for half of the initial number of nuclei present to decay in a first-order reaction. (For more information on half-life, see Section 14.5.) An isotope's half-life can range from fractions of a second to billions of years and, among other applications, can be used to measure the age of ancient objects. Example 1 and its corresponding exercise review the calculations involving radioactive decay rates and half-lives.

### Example 24.1.1

Fort Rock Cave in Oregon is the site where archaeologists discovered several Indian sandals, the oldest ever found in Oregon. Analysis of the $^{14}C$ content of the sagebrush used to make the sandals gave an average decay rate of 5.1 disintegrations per minute (dpm) per gram of carbon. The current $^{14}C/^{12}C$ ratio in living organisms is $1.3 \times 10^{-12}$, with a decay rate of 15 dpm/g C. How long ago was the sagebrush in the sandals cut? The half-life of $^{14}C$ is 5730 yr.

**Given:** radioisotope, current $^{14}C/^{12}C$ ratio, initial decay rate, final decay rate, and half-life

**Asked for:** age

**Strategy:**

**A** Use Equation 14.5.5 to calculate $N_0/N$, the ratio of the number of atoms of $^{14}C$ originally present in the sample to the number of atoms now present.

**B** Substitute the value for the half-life of $^{14}C$ into Equation 14.5.3 to obtain the rate constant for the reaction.

**C** Substitute the calculated values for $N_0/N$ and the rate constant into Equation 14.5.7 to obtain the elapsed time $t$.

**Solution:**

We can use the integrated rate law for a first-order nuclear reaction (Equation 14.5.7 to calculate the amount of time that has passed since the sagebrush was cut to make the sandals:

$$ln\frac{N}{N_o} = -kt \tag{24.2.1}$$

**A** From Equation 14.5.5, we know that $A = kN$. We can therefore use the initial and final activities ($A_0$ = 15 and $A$ = 5.1) to calculate $N_0/N$:

$$\frac{A_o}{A} = \frac{kN_o}{kN} = \frac{N_o}{N} = dfrac1.55.1 \tag{24.2.2}$$

**B** Now we can calculate the rate constant $k$ from the half-life of the reaction (5730 yr) using Equation 14.5.3:

$$t_{1/2} = \frac{0.693}{k} \tag{24.2.3}$$

Rearranging this equation to solve for $k$,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ yr} = 1.21 \times 10^{-4}\ yr^{-1} \tag{24.2.4}$$

**C** Substituting the calculated values into the equation for $t$,

$$t = \frac{ln\,(N/N_o)}{k} = \frac{ln\,(15/5.1)}{1.21 \times 10^{-4}\ yr^{-1}} = 8900\ yr \tag{24.2.5}$$

Thus the sagebrush in the sandals is about 8900 yr old.

Exercise

While trying to find a suitable way to protect his own burial chamber, the ancient Egyptian pharaoh Sneferu developed the pyramid, a burial structure that protected desert graves from thieves and exposure to wind. Analysis of the $^{14}C$ content of several items in pyramids built during his reign gave an average decay rate of 8.6 dpm/g C. When were the objects in the chamber created?

**Answer:** about 4600 yr ago, or about 2600 BC

## Nuclear Stability

As discussed in Chapter 1, the nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the strong nuclear forceAn extremely powerful but very short-range attractive force between nucleons that keeps the nucleus of an atom from flying apart (due to electrostatic repulsions between protons)., an extremely powerful but very short-range attractive force between nucleons (Figure 24.1.1 ). All stable nuclei except the hydrogen-1 nucleus ($^1H$) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

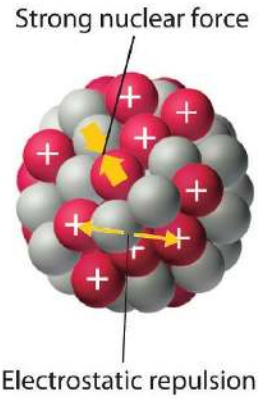



Figure 24.1.1 Competing Interactions within the Atomic **Nucleus** Eectrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 24.1.2. The stable isotopes form a "peninsula of stability" in a "sea of instability." Only two stable isotopes, $^{1}H$ and $^{3}He$, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $^{4}He$, $^{10}B$, $^{40}Ca$. All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with $Z >$ 83 are unstable and radioactive.

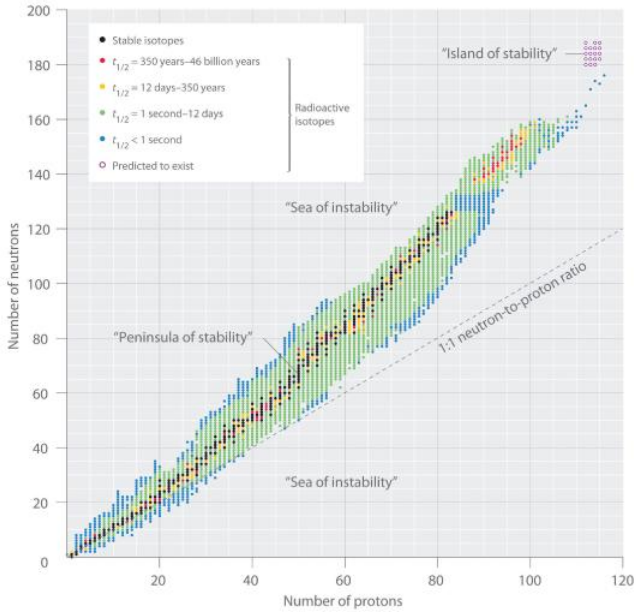



Figure 24.1.2 The Relationship between Nuclear Stability and the Neutron-to-Proton **Ratio** In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized.

Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

As shown in Figure 24.1.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in

especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin ($Z$ = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium ($Z$ = 49) and antimony ($Z$ = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be "doubly magic" and are even more stable. Examples of elements with doubly magic nuclei are $^{4}$He with 2 protons and 2 neutrons, and $^{208}$Pb with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

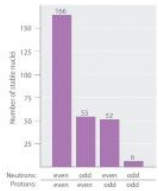


Figure 24.1.3 The Relationship between the Number of Protons and the Number of Neutrons and Nuclear **Stability** Most stable nuclei contain even numbers of both neutrons and protons.

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 24.1.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

### Example 24.1.2

Classify each nuclide as stable or radioactive.

1. $^{30}_{15}P$
2. $^{98}_{43}Tc$
3. tin-118
4. $^{239}_{94}Pu$

**Given:** mass number and atomic number

**Asked for:** predicted nuclear stability

**Strategy:**

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

**Solution:**

1. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 24.1.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}P$ is predicted to be radioactive, and it is.
2. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}Tc$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that $^{98}_{43}Tc$ might be stable. However, $^{98}_{43}Tc$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}Tc$ is predicted to be radioactive, and it is.
3. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an *even* number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}Sn$ should be particularly stable.
4. This nuclide has an atomic number of 94. Because all nuclei with $Z$ > 83 are unstable, $^{239}_{94}Sn$must be radioactive.

Exercise

Classify each nuclide as stable or radioactive.

1. $^{232}_{90}Th$
2. $^{40}_{20}Ca$
3. $^{15}_{8}O$
4. $^{139}_{57}La$

**Answer**

1. radioactive
2. stable
3. radioactive
4. stable

## Superheavy Elements

In addition to the "peninsula of stability," Figure 24.1.2 shows a small "island of stability" that is predicted to exist in the upper right corner. This island corresponds to the superheavy elementsAn element with an atomic number near the magic number of 126., with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with $Z$ = 114 and $Z$ = 116 have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an "eternity" by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with $A$ = 292 that was found in $^{232}$Th. With an estimated half-life greater than $10^8$ years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with $Z$ = 122. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

### Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

### Key Takeaway

- Nuclei with magic numbers of neutrons or protons are especially stable, as are those nuclei that are doubly magic.

### Conceptual Problems

1. What distinguishes a nuclear reaction from a chemical reaction? Use an example of each to illustrate the differences.
2. What do chemists mean when they say a substance is *radioactive*?
3. What characterizes an isotope? How is the mass of an isotope of an element related to the atomic mass of the element shown in the periodic table?
4. In a typical nucleus, why does electrostatic repulsion between protons not destabilize the nucleus? How does the neutron-to-proton ratio affect the stability of an isotope? Why are all isotopes with $Z$ > 83 unstable?
5. What is the significance of a *magic number* of protons or neutrons? What is the relationship between the number of stable isotopes of an element and whether the element has a magic number of protons?
6. Do you expect Bi to have a large number of stable isotopes? Ca? Explain your answers.
7. Potassium has three common isotopes, $^{39}$K, $^{40}$K, and $^{41}$K, but only potassium-40 is radioactive (a beta emitter). Suggest a reason for the instability of $^{40}$K.
8. Samarium has 11 relatively stable isotopes, but only 4 are nonradioactive. One of these 4 isotopes is $^{144}$Sm, which has a lower neutron-to-proton ratio than lighter, radioactive isotopes of samarium. Why is $^{144}$Sm more stable?

## Answers

1.
2.
3.
4.
5. Isotopes with magic numbers of protons and/or neutrons tend to be especially stable. Elements with magic numbers of protons tend to have more stable isotopes than elements that do not.
6.
7. Potassium-40 has 19 protons and 21 neutrons. Nuclei with odd numbers of both protons and neutrons tend to be unstable. In addition, the neutron-to-proton ratio is very low for an element with this mass, which decreases nuclear stability.
8.

## Numerical Problems

1. Write the nuclear symbol for each isotope using notation.
    1. chlorine-39
    2. lithium-8
    3. osmium-183
    4. zinc-71
2. Write the nuclear symbol for each isotope using $^{A}_{Z}X$ notation.
    1. lead-212
    2. helium-5
    3. oxygen-19
    4. plutonium-242
3. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.
    1. iron-57
    2. $^{185}W$
    3. potassium-39
    4. $^{131}Xe$
4. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.
    1. technetium-99*m*
    2. $^{140}La$
    3. radium-227
    4. $^{208}Bi$
5. Which of these nuclides do you expect to be radioactive? Explain your reasoning.
    1. $^{20}ne$
    2. tungsten-184
    3. $^{106}Ti$
6. Which of these nuclides do you expect to be radioactive? Explain your reasoning.
    1. $^{107}Ag$
    2. $^{50}V$
    3. lutetium-176

## Answers

1. 1. $^{39}_{17}Cl$
    2. $^{8}_{3}Li$

3. $^{183}_{76}Os$
4. $^{71}_{30}Zn$

2.

3. 1. 26 protons; 31 neutrons; 1.19
   2. 74 protons; 111 neutrons; 1.50
   3. 19 protons; 20 neutrons; 1.05
   4. 54 protons; 77 neutrons; 1.43

4.
5.
6.

## Contributors

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# 24.3: Nuclear Reactions

**Learning Objectives**

- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> *Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.*

## Classes of Radioactive Nuclei

The three general classes of radioactive nuclei are characterized by a different decay process or set of processes:

1. **Neutron-rich nuclei.** The nuclei on the upper left side of the band of stable nuclei have a neutron-to-proton ratio that is too high to give a stable nucleus. These nuclei decay by a process that *converts a neutron to a proton*, thereby *decreasing* the neutron-to-proton ratio.
2. **Neutron-poor nuclei.** Nuclei on the lower right side of the band of stable nuclei have a neutron-to-proton ratio that is too low to give a stable nucleus. These nuclei decay by processes that have the net effect of *converting a proton to a neutron*, thereby *increasing* the neutron-to-proton ratio.
3. **Heavy nuclei.** With very few exceptions, heavy nuclei (those with $A \geq 200$) are intrinsically unstable regardless of the neutron-to-proton ratio, and all nuclei with $Z > 83$ are unstable. This is presumably due to the cumulative effects of electrostatic repulsions between the large number of positively charged protons, which cannot be totally overcome by the strong nuclear force, regardless of the number of neutrons present. Such nuclei tend to decay by emitting an α particle (a helium nucleus, $^{4}_{2}\mathrm{He}$, which decreases the number of protons and neutrons in the original nucleus by 2. Because the neutron-to-proton ratio in an α particle is 1, the net result of alpha emission is an increase in the neutron-to-proton ratio.

> *Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus.*

## Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the $^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table 24.3.1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 24.3.1: Nuclear Decay Emissions and Their Symbols

| Identity | Symbol | Charge | Mass (amu) |
|---|---|---|---|
| helium nucleus | ${}^{4}_{2}\alpha$ | +2 | 4.001506 |
| electron | ${}^{0}_{-1}\beta$ or $\beta^{-}$ | −1 | 0.000549 |
| photon | ${}^{0}_{0}\gamma$ | — | — |
| neutron | ${}^{1}_{0}\mathrm{n}$ | 0 | 1.008665 |
| proton | ${}^{1}_{1}\mathrm{p}$ | +1 | 1.007276 |
| positron | ${}^{0}_{+1}\beta$ or $\beta^{+}$ | +1 | 0.000549 |

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = -1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both $A$ and $Z$ are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to $\mathrm{e}^{-}$, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to $\beta^{-}$, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 24.3.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

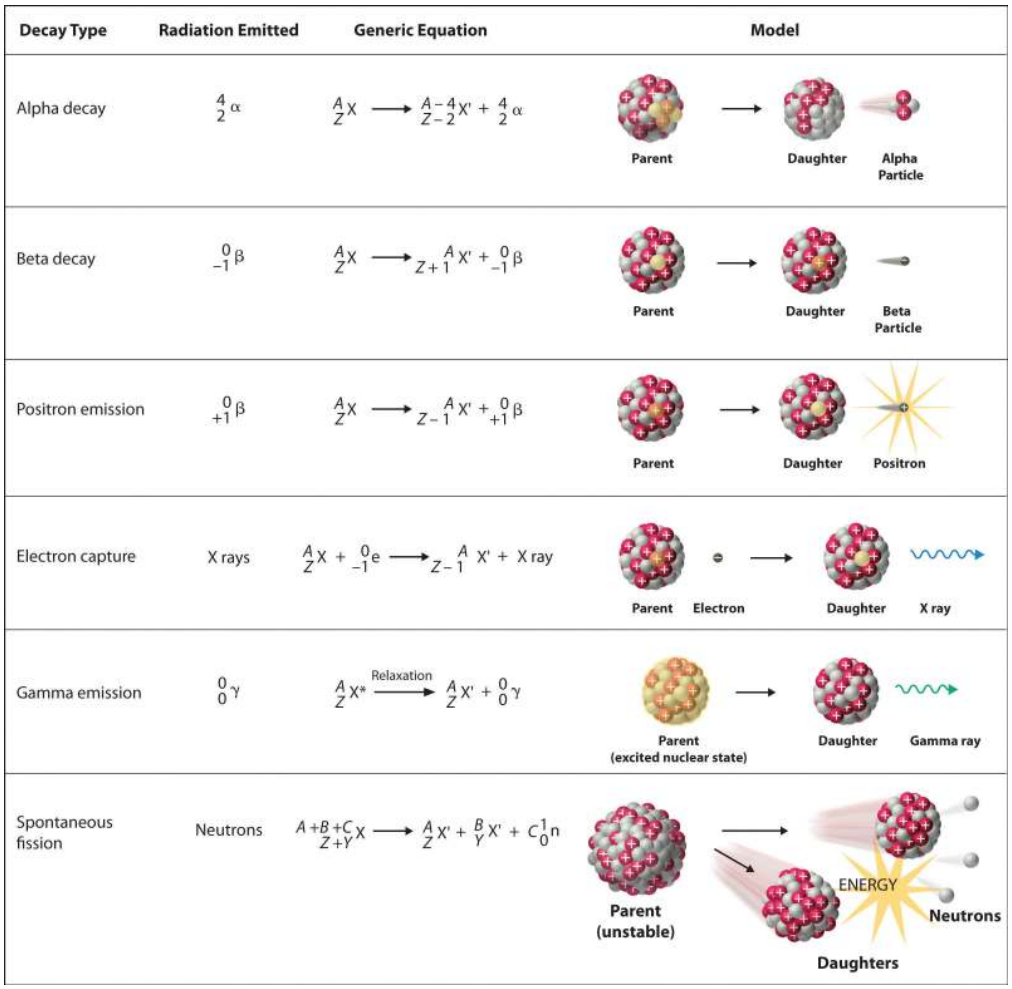



Figure 24.3.1: Common Modes of Nuclear Decay

## Alpha Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{{}^{4}_{2}\alpha} \tag{24.3.1}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{24.3.2}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

## Beta Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{24.3.3}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{24.3.4}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta \tag{24.3.5}$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

## Positron Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{24.3.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}} \tag{24.3.7}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta^{+} \tag{24.3.8}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

## Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{24.3.9}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} + \underset{\text{electron}}{{}^{0}_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \text{x-ray} \tag{24.3.10}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of

the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}\text{Fe} \xrightarrow{\text{EC}} {}^{55}_{25}\text{Mn} + \text{x-ray} \tag{24.3.11}$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow {}^{55}_{25}\text{Mn} + \text{x-ray} \tag{24.3.12}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

## Gamma Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** ($\gamma$) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\text{U} \rightarrow \underbrace{^{234}_{90}\text{Th}^*}_{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma \tag{24.3.13}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^* \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma \tag{24.3.14}$$

or more generally,

$$^{A}_{Z}\text{X}^* \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma \tag{24.3.15}$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

## Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4{}^{1}_{0}\text{n} \tag{24.3.16}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

### ✔ Example 24.3.1

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$
b. the decay of $^{201}_{80}\text{Hg}$ by electron capture

c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

**Given:** radioactive nuclide and mode of decay

**Asked for:** balanced nuclear equation

**Strategy:**

**A** Identify the reactants and the products from the information given.

**B** Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

**Solution**

a.

**A** We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as $^{A}_{Z}\mathrm{X}$:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta \tag{24.3.17}$$

**B** Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta \tag{24.3.18}$$

b.

**A** We know the identities of both reactants: $^{201}_{80}\mathrm{Hg}$ and an inner electron, $^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X}$$

**B** Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au}$$

c.

**A** As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta$$

**B** The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta$$

## ? Exercise 24.3.1

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\mathrm{W}$

**Answer**

a. $^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$
b. $^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$
c. $^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

### Example 24.3.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

**Given:** nuclide

**Asked for:** type of nuclear decay

**Strategy:**

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

**Solution**

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

### Exercise 24.3.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

**Answer**

a. beta decay
b. positron emission or electron capture
c. alpha decay

## Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases *Z* by only 2, and positron emission or electron capture decreases *Z* by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and

beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 24.3.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

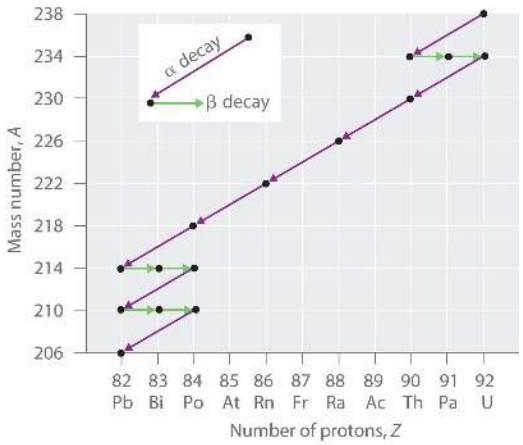



Figure 24.3.1: A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

## Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \tag{24.3.19}$$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{24.3.20}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 24.3.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{24.3.21}$$

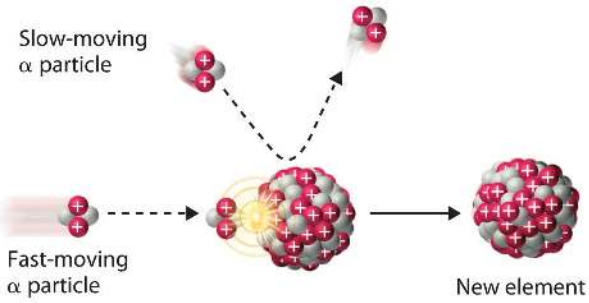



Figure 24.3.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

## Example 24.3.3

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each $^{27}$Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

**Given:** reactants in a nuclear transmutation reaction

**Asked for:** product nuclide and balanced nuclear equation

**Strategy:**

**A** Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

**B** Write the balanced nuclear equation for the reaction.

**Solution**

**A** Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum ($Z$ = 13) will be converted to phosphorus ($Z$ = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

**B** The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n} \tag{24.3.22}$$

## Exercise 24.3.1

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei ($^{2}_{1}\mathrm{H}$) produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

**Answer**

neutron, ${}^{1}_{0}\text{n}$; ${}^{96}_{42}\text{Mo} + {}^{2}_{1}\text{H} \rightarrow {}^{97}_{43}\text{Tc} + {}^{1}_{0}\text{n}$

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of $Z$, such as the isotopes of uranium ($Z$ = 92) and plutonium ($Z$ = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as ${}^{235}_{92}\text{U}$ and ${}^{239}_{94}\text{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 24.3.3:

$$ {}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{236}_{92}\text{U} \rightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3{}^{1}_{0}\text{n} \tag{24.3.23} $$

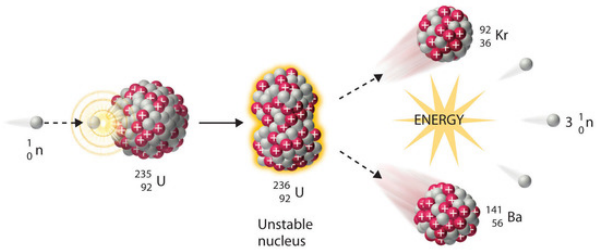



Figure 24.3.4: Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 24.3.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 24.3.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

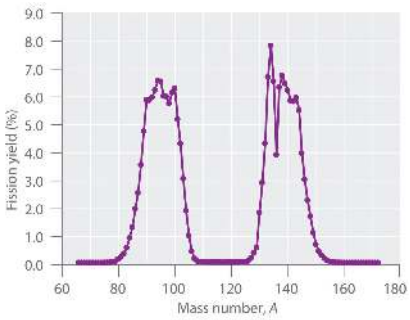



Figure 24.3.5: Mass Distribution of Nuclear Fission Products of $^{235}$U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for235U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

## Synthesis of Transuranium Elements

Uranium ($Z$ = 92) is the heaviest naturally occurring element. Consequently, all the elements with $Z$ > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium ($Z$ = 93), which was synthesized in 1940 by bombarding a $^{238}$U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a $^{238}$U nucleus to form $^{239}$U, which is unstable and undergoes beta decay to produce $^{239}$Np:

$$ {}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{239}_{92}\text{U} \rightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\beta $$

Subsequent beta decay of $^{239}$Np produces the second transuranium element, plutonium ($Z$ = 94):

$$ {}^{239}_{93}\text{Np} \rightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\beta $$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 24.3.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 24.3.2: Some Reactions Used to Synthesize Transuranium Elements

| |
|---|
| $^{239}_{94}\text{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$ |
| $^{239}_{94}\text{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\text{Am} + {}^{1}_{1}\text{p} + {}^{1}_{0}\text{n}$ |
| $^{242}_{96}\text{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\text{Bk} + {}^{1}_{1}\text{p} + 2{}^{1}_{0}\text{n}$ |
| $^{253}_{99}\text{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$ |
| $^{238}_{92}\text{U} + {}^{12}_{6}\text{C} \rightarrow {}^{246}_{98}\text{Cf} + 4{}^{1}_{0}\text{n}$ |
| $^{252}_{98}\text{Cf} + {}^{10}_{5}\text{B} \rightarrow {}^{256}_{103}\text{Lr} + 6{}^{1}_{0}\text{n}$ |

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 24.3.6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

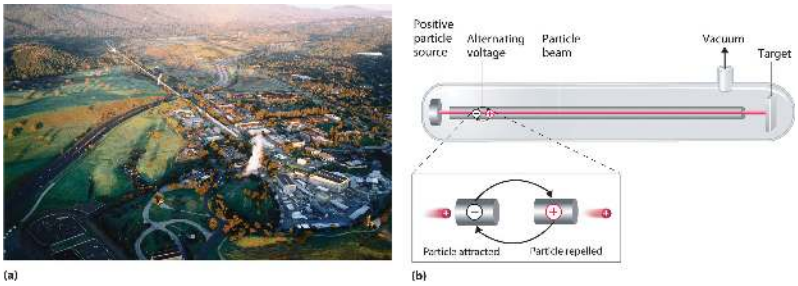



Figure 24.3.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

## Summary

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, ${}^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as

the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

## Key Takeaway

Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

## Key Equations

**alpha decay**

Equation 20.1: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha$

**beta decay**

Equation 20.4: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta$

**positron emission**

Equation 20.7: ${}^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta$

**electron capture**

Equation 20.10: ${}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray}$

**gamma emission**

Equation 20.15: ${}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$

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# 24.4: The Interaction of Nuclear Radiation with Matter

**Learning Objectives**

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus ($He^{2+}$) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

## Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. Nonionizing radiationRadiation that is relatively low in energy. When it collides with an atom in a molecule or ion, most or all of its energy can be absorbed without causing a structural or a chemical change. is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, ionizing radiationRadiation of a high enough energy to transfer some as it passes through matter to one or more atoms with which it collides. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions. is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$atom + ionizing\ radiation \rightarrow ion^{+} + e^{-}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 24.3.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle: 1 MeV/particle = 96 billion J/mol.



Figure 24.3.1 Radiation **Damage** When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue.

## The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 24.3.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

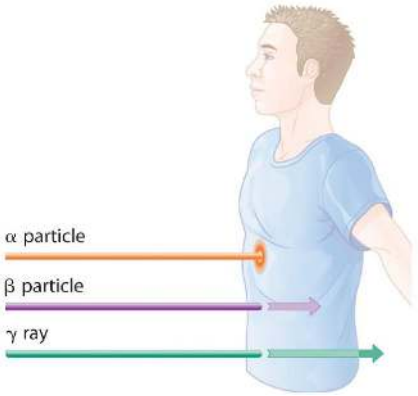



Figure 24.3.2 Depth of Penetration of Ionizing **Radiation**The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed.

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 24.3.1

**Table 24.3.1 Some Properties of Ionizing Radiation**

| Type | Energy Range (MeV) | Penetration Distance in Water* | Penetration Distance in Air* |
|---|---|---|---|
| α particles | 3–9 | < 0.05 mm | < 10 cm |
| β particles | ≤ 3 | < 4 mm | 1 m |
| x-rays | $<10^{-2}$ | < 1 cm | < 3 m |
| γ rays | $10^{-2}$–$10^{1}$ | < 20 cm | > 3 m |

*Distance at which half of the radiation has been absorbed.

## Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

There are many different ways to measure radiation exposure, or the *dose*. The roentgen (R)A unit that describes the amount of energy absorbed by dry air and measures the radiation exposure or dose., which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of $2.58 \times 10^{-4}$ C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed

by *tissues*, not air. The most common unit used to measure the effects of radiation on biological tissue is the rad (radiation absorbed dose)A unit used to measure the effects of radiation on biological tissues; the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter.; the SI equivalent is the *gray* (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\ rad = 0.010\ J/kg \quad 1\ Gy = 1\ J/kg$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = $1.4 \times 10^{-4}$ J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a $3.8 \times 10^{-5}$ g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the rem (roentgen equivalent in man)A unit that describes the actual amount of tissue damage caused by a given amount of radiation and equal to the number of rads multiplied by the RBE. was devised to describe the *actual* amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the *RBE* (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in *millirems* (1 mrem = $10^{-3}$ rem).

## Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 24.3.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

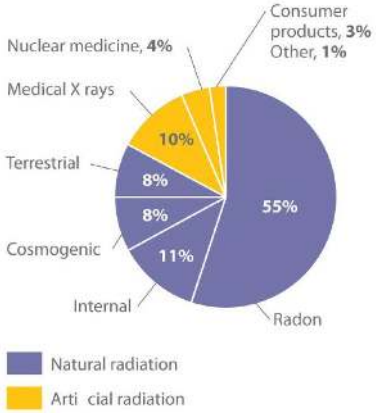



Figure 24.3.3 The Radiation Exposure of a Typical Adult in the United **States** The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each.

Data source: Office of Civilian Radioactive Waste Management

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as $^{14}C$:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}p$$

The carbon atoms react with oxygen atoms to form $CO_2$, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in $1 \times 10^{12}$ of the carbon atoms in our bodies is radioactive $^{14}C$, which decays by beta emission. About 5000

$^{14}C$ nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium ($^{3}H$) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to $^{14}C$ is estimated to be 1 mrem/yr, while that due to $^{3}H$ is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as $^{232}Th$ and $^{238}U$, as well as radioactive daughter isotopes, such as $^{226}Ra$. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the $K^+$ ion. Naturally occurring potassium contains 0.0117% $^{40}K$, which decays by emitting both a β particle and a γ ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 $^{40}K$ nuclei disintegrated in your body.

By far the most important source of background radiation is *radon*, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of $^{238}U$, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, $^{222}Rn$ undergoes two successive alpha-decay events to give $^{214}Pb$:

$$^{222}_{86}Rn \rightarrow ^{218}_{84}Po + ^{4}_{2}\alpha \rightarrow ^{214}_{82}Pb + ^{4}_{2}\alpha$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of $^{218}Po$ releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The $^{218}Po$ isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

## Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium ($^{3}H$) and promethium ($^{147}Pr$), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

### Example 24.3.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring $^{40}K$ in his or her body, which contains about 140 g of potassium (as the $K^+$ ion). The natural abundance of $^{40}K$ is 0.0117%. Each 1.00 mol of $^{40}K$ undergoes $1.05 \times 10^{7}$ decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

**Given:** mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

**Asked for:** annual radiation dose in rads

**Strategy:**

**A** Calculate the number of moles of $^{40}$K present using its mass, molar mass, and natural abundance.

**B** Determine the number of decays per year for this amount of $^{40}$K.

**C** Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

**Solution:**

**A** The number of moles of $^{40}$K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as $^{40}$K divided by the atomic mass of $^{40}$K:

$$moles\ ^{40}K = 140\ \cancel{gK} \times \frac{0.0117\ mol^{40}K}{100\ \cancel{mol\ K}} \times \frac{1\ \cancel{mol\ K}}{40.0\ \cancel{gK}} = 4.10 \times 10^{-4}\ mol\ ^{40}K$$

**B** We are given the number of atoms of $^{40}$K that decay per second in 1.00 mol of $^{40}$K, so the number of decays per year is as follows:

$$\dfrac{decays}{year} = 4.10 \times 10^{-4}\ mol\ ^{40}K \times \dfrac{1.05 \times 10^{7}\ decays/\cancel{s}}{1\ \cancel{mol\ ^{40}K}} \times \dfrac{60\ \cancel{s}}{1\ \cancel{min}} \times \dfrac{60\ \cancel{min}}{1\ \cancel{h}} \times \dfrac{24\ \cancel{h}}{1\ \cancel{day}} \times \dfrac{365\ \cancel{day}}{1\ yr}$$

**C** The total energy the body receives per year from the decay of $^{40}$K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$total\ energy\ per\ year = \frac{1.36 \times 10^{11}\ \cancel{decays}}{yr} \times \frac{1.32\ \cancel{MeV}}{\cancel{decay}} \times \frac{10^{6}\ \cancel{eV}}{\cancel{MeV}} \times \frac{1.602 \times 10^{-19}\ J}{\cancel{eV}}$$

$$= 2.87 \times 10^{-2}\ J/yr$$

We use the definition of the rad (1 rad = $10^{-2}$ J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$radiation\ dose\ per\ year = \frac{2.87 \times 10^{-2}\ \cancel{J}/yr}{70\ \cancel{kg}} \times \frac{1\ rad}{1 \times 10^{-2}\ \cancel{J}/\cancel{kg}}$$

$$= 4.10 \times 10^{-2}\ rad/yr = 41\ mrad/yr$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise

Because strontium is chemically similar to calcium, small amounts of the $Sr^{2+}$ ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of $Ca^{2+}$. Consequently, the radioactive strontium ($^{90}$Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of $^{90}$Sr undergoes $4.55 \times 10^{14}$ decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were $^{90}$Sr?

**Answer:** $5.7 \times 10^{3}$ rad/yr (which is 10 times the fatal dose)

## Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 24.3.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

**Table 24.3.2 The Effects of a Single Radiation Dose on a 70 kg Human**

| Dose (rem) | Symptoms/Effects |
|---|---|
| < 5 | no observable effect |
| 5–20 | possible chromosomal damage |
| 20–100 | temporary reduction in white blood cell count |
| 50–100 | temporary sterility in men (up to a year) |
| 100–200 | mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded |
| > 300 | permanent sterility in women |
| > 500 | fatal to 50% within 30 days; destruction of bone marrow and intestine |
| > 3000 | fatal within hours |

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 24.3.4, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that *all* exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

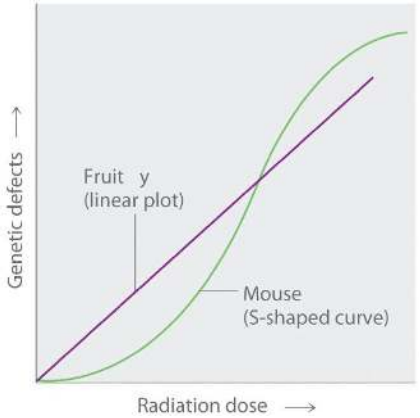



Figure 24.3.4 Two Possible Relationships between the Number of Genetic Defects and Radiation **Exposure** Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate.

## Summary

The effects of radiation on matter depend on the energy of the radiation. **Nonionizing radiation** is relatively low in energy, and the energy is transferred to matter in the form of heat. **Ionizing radiation** is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the **roentgen (R)**, the amount of energy absorbed by dry air, and the **rad (radiation absorbed dose)**, the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The **rem (roentgen equivalent in man)** measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include *cosmic radiation*, consisting of high-energy particles and γ rays emitted by the sun and other stars; *cosmogenic radiation*, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and *terrestrial radiation*, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

## Key Takeaway

- Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive.

## Key Equation

**rad**

Equation 24.3.2: 1 rad = 0.01 J/kg

## Conceptual Problems

1. Why are many radioactive substances warm to the touch? Why do many radioactive substances glow?
2. Describe the differences between nonionizing and ionizing radiation in terms of the intensity of energy emitted and the effect each has on an atom or molecule after collision. Which nuclear decay reactions are more likely to produce ionizing radiation? nonionizing radiation?
3. Would you expect nonionizing or ionizing radiation to be more effective at treating cancer? Why?
4. Historically, concrete shelters have been used to protect people from nuclear blasts. Comment on the effectiveness of such shelters.
5. Gamma rays are a very high-energy radiation, yet α particles inflict more damage on biological tissue. Why?
6. List the three primary sources of naturally occurring radiation. Explain the factors that influence the dose that one receives throughout the year. Which is the largest contributor to overall exposure? Which is the most hazardous?
7. Because radon is a noble gas, it is inert and generally unreactive. Despite this, exposure to even low concentrations of radon in air is quite dangerous. Describe the physical consequences of exposure to radon gas. Why are people who smoke more susceptible to these effects?
8. Most medical imaging uses isotopes that have extremely short half-lives. These isotopes usually undergo only one kind of nuclear decay reaction. Which kind of decay reaction is usually used? Why? Why would a short half-life be preferred in these cases?
9. Which would you prefer: one exposure of 100 rem, or 10 exposures of 10 rem each? Explain your rationale.

## Answers

1.
2.
3. Ionizing radiation is higher in energy and causes greater tissue damage, so it is more likely to destroy cancerous cells.
4.
5.
6.
7.

8.

9. Ten exposures of 10 rem are less likely to cause major damage.

## Numerical Problems

1. A 2.14 kg sample of rock contains 0.0985 g of uranium. How much energy is emitted over 25 yr if 99.27% of the uranium is $^{238}U$, which has a half-life of $4.46 \times 10^9$ yr, if each decay event is accompanied by the release of 4.039 MeV? If a 180 lb individual absorbs all of the emitted radiation, how much radiation has been absorbed in rads?

2. There is a story about a “radioactive boy scout” who attempted to convert thorium-232, which he isolated from about 1000 gas lantern mantles, to uranium-233 by bombarding the thorium with neutrons. The neutrons were generated via bombarding an aluminum target with α particles from the decay of americium-241, which was isolated from 100 smoke detectors. Write balanced nuclear reactions for these processes. The “radioactive boy scout” spent approximately 2 h/day with his experiment for 2 yr. Assuming that the alpha emission of americium has an energy of 5.24 MeV/particle and that the americium-241 was undergoing $3.5 \times 10^6$ decays/s, what was the exposure of the 60.0 kg scout in rads? The intrepid scientist apparently showed no ill effects from this exposure. Why?

## Contributors

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Modified by Joshua B. Halpern

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# 24.5: Thermodynamic Stability of the Atomic Nucleus

**Learning Objectives**

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

## Mass–Energy Balance

The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \tag{24.5.1}$$

where c is the speed of light ($2.998 \times 10^8$ m/s), and E and m are expressed in units of joules and kilograms, respectively. Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 20.27, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5\ \mathrm{kJ/mol} \tag{24.5.2}$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, ΔE ≈ ΔH. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \tag{24.5.3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{24.5.4}$$

Because 1 J = 1 (kg·m$^2$)/s$^2$, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ \mathrm{kJ/mol}}{(2.998 \times 10^8\ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8\ \mathrm{m/s})^2} = -4.38 \times 10^{-12}\ \mathrm{kg/mol} \tag{24.5.5}$$

This is a mass change of about $3.6 \times 10^{-10}$ g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of $^{14}$C to $^{14}$N and an electron (a β particle), there is a much larger change in mass:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{24.5.6}$$

We can use the experimentally measured masses of subatomic particles and common isotopes to calculate the change in mass directly. The reaction involves the conversion of a neutral $^{14}$C atom to a positively charged $^{14}$N ion (with six, not seven, electrons)

and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral $^{14}$N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral $^{14}$N atom (14.003074 amu) and the mass of a $^{14}$C atom (14.003242 amu):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{24.5.7}$$
$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \tag{24.5.8}$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of $^{14}$C is −0.000168 g = $-1.68 \times 10^{-4}$ g = $-1.68 \times 10^{-7}$ kg. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 \tag{24.5.9}$$
$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^7 \text{ kJ} \tag{24.5.10}$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of $^{14}$C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = $10^3$ eV), megaelectronvolts (1 MeV = $10^6$ eV), and even gigaelectronvolts (1 GeV = $10^9$ eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of $^{14}$C is thus

$$(-1.68 \times 10^{-4} \text{ amu}) \left( \frac{931 \text{ MeV}}{\text{amu}} \right) = -0.156 \text{ MeV} = -156 \text{ keV} \tag{24.5.11}$$

## Example 24.5.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of $^{238}$U to $^{234}$Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

**Given:** nuclear decay reaction

**Asked for:** changes in mass and energy

**Strategy:**

**A** Use the mass values in Table 20.1 to calculate the change in mass for the decay reaction in atomic mass units.

**B** Use Equation 20.30 to calculate the change in energy in joules per mole.

**C** Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

**Solution**

**A** Using particle and isotope masses from Table 20.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } ^{234}\text{Th} + \text{mass } ^4_2\text{He}) - \text{mass } ^{238}\text{U} \tag{24.5.12}$$
$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \tag{24.5.13}$$

**B** Thus the change in mass for 1 mol of $^{238}$U is −0.004584 g or $-4.584 \times 10^{-6}$ kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 = -4.120 \times 10^{11} \text{ J/mol}$$

**C** The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3} \text{ amu} \times \frac{931 \text{ MeV}}{\text{amu}} \times \frac{1 \times 10^6 \text{ eV}}{1 \text{ MeV}} = -4.27 \times 10^6 \text{ eV/atom}$$

**? Exercise 24.5.1**

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium ($^3$H) to $^3$He and a β particle.

**Answer**

$\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^6$ kJ/mol = −19 keV/atom

## Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 ($^1$H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium ($^2$H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$m_{^2\mathrm{H}} = m_{\mathrm{neutron}} + m_{\mathrm{proton}} + m_{\mathrm{electron}} \tag{24.5.14}$$

$$= 1.008665\ \mathrm{amu} + 1.007276\ \mathrm{amu} + 0.000549\ \mathrm{amu} = 2.016490\ \mathrm{amu} \tag{24.5.15}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 24.5.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 21.2.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.

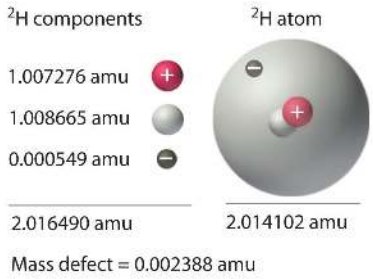



Figure 24.5.1: Nuclear Binding Energy in Deuterium. *The mass of a $^2$H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.*

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 24.5.2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., $^4$He, $^{12}$C, and $^{16}$O). As mentioned earlier, these are particularly stable combinations.

Because the maximum binding energy per nucleon is reached at $^{56}$Fe, all other nuclei are thermodynamically unstable with regard to the formation of $^{56}$Fe. Consequently, heavier nuclei (toward the right in 24.5.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 24.5.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

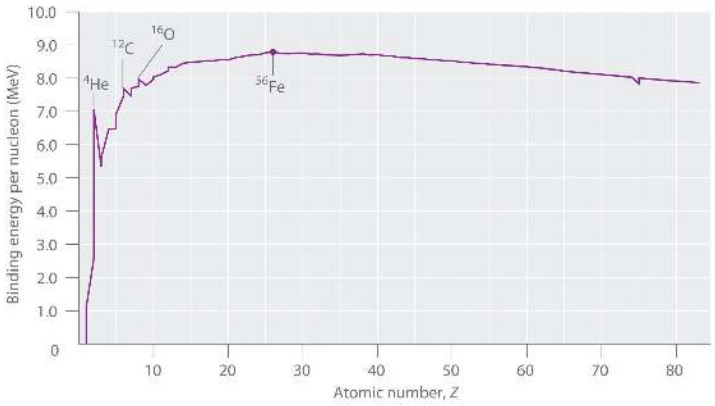



Figure 24.5.3: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Heavier nuclei spontaneously undergo nuclear reactions that *decrease* their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that *increase* their atomic number.

## Example 24.5.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for $^{56}$Fe. The experimental mass of the nuclide is given in Table A4.

**Given:** nuclide and mass

**Asked for:** nuclear binding energy and binding energy per nucleon

**Strategy:**

**A** Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of $^{1}$H atoms (because its mass is the same as the mass of one electron and one proton).

**B** Calculate the mass defect by subtracting the experimental mass from the calculated mass.

**C** Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

**Solution**

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 $^{1}$H atoms, we can calculate the sum of the masses more quickly as follows:

$$\text{calculated mass} = 26(\text{mass } {}^{1}_{1}\text{H}) + 30(\text{mass } {}^{1}_{0}\text{n}) \tag{24.5.16}$$

$$= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400 \text{ amu} \tag{24.5.17}$$

$$\text{experimental mass} = 55.934938 \tag{24.5.18}$$

**B** We subtract to find the mass defect:

$$\text{mass defect} = \text{calculated mass} - \text{experimental mass} \tag{24.5.19}$$

$$= 56.463400 \text{ amu} - 55.934938 \text{ amu} = 0.528462 \text{ amu} \tag{24.5.20}$$

**C** The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

## Exercise 24.5.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for $^{238}$U.

**Answer** 1800 MeV/$^{238}$U; 7.57 MeV/nucleon

## Nuclear Fission and Fusion

N**uclear fission** is the splitting of a heavy nucleus into two lighter ones. Fission was discovered in 1938 by the German scientists Otto Hahn, Lise Meitner, and Fritz Strassmann, who bombarded a sample of uranium with neutrons in an attempt to produce new elements with Z > 92. They observed that lighter elements such as barium (Z = 56) were formed during the reaction, and they realized that such products had to originate from the neutron-induced fission of uranium-235:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{24.5.21}$$

This hypothesis was confirmed by detecting the krypton-92 fission product. The nucleus usually divides asymmetrically rather than into two equal parts, and the fission of a given nuclide does not give the same products every time.

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reactions known as a **nuclear chain reaction** can result (Figure 24.5.3). For example, the fission of $^{235}$U releases two to three neutrons per fission event. If absorbed by other $^{235}$U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a generation. Experimentally, it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the **critical mass**. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available from which neutrons can escape, and on the identity of the isotope. If the mass of the fissile isotope is greater than the critical mass, then under the right conditions, the resulting supercritical mass can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.

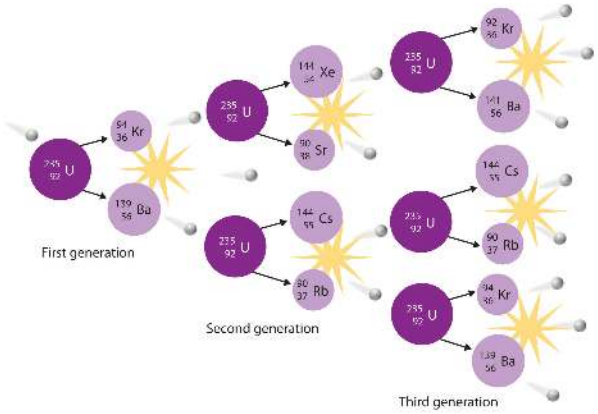



Figure 24.5.3: A Nuclear Chain Reaction. The process is initiated by the collision of a single neutron with a $^{235}$U nucleus, which undergoes fission, as shown in Figure 20.6. Because each neutron released can cause the fission of another $^{235}$U nucleus, the rate of a fission reaction accelerates geometrically. Each series of events is a generation.

**Nuclear fusion**, in which two light nuclei combine to produce a heavier, more stable nucleus, is the opposite of nuclear fission. As in the nuclear transmutation reactions discussed in Section 20.2, the positive charge on both nuclei results in a large electrostatic energy barrier to fusion. This barrier can be overcome if one or both particles have sufficient kinetic energy to overcome the electrostatic repulsions, allowing the two nuclei to approach close enough for a fusion reaction to occur. The principle is similar to adding heat to increase the rate of a chemical reaction. As shown in the plot of nuclear binding energy per nucleon versus atomic number in Figure 21.2.3, fusion reactions are most exothermic for the lightest element. For example, in a typical fusion reaction, two deuterium atoms combine to produce helium-3, a process known as deuterium–deuterium fusion (D–D fusion):

$$2{}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{24.5.22}$$

In another reaction, a deuterium atom and a tritium atom fuse to produce helium-4 (Figure 24.5.4), a process known as deuterium–tritium fusion (D–T fusion):

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{24.5.23}$$

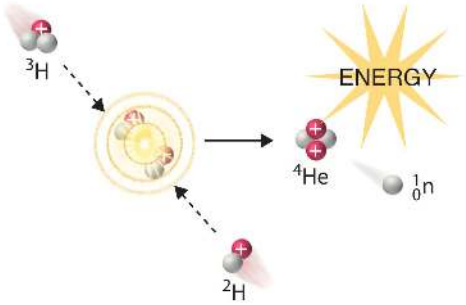



Figure 24.5.4: Nuclear Fusion. In a nuclear fusion reaction, lighter nuclei combine to produce a heavier nucleus. As shown, fusion of $^3$H and $^2$H to give $^4$He and a neutron releases an enormous amount of energy. In principle, nuclear fusion can produce much more energy than fission, but very high kinetic energy is required to overcome electrostatic repulsions between the positively charged nuclei and initiate the fusion reaction.

Initiating these reactions, however, requires a temperature comparable to that in the interior of the sun (approximately $1.5 \times 10^7$ K). Currently, the only method available on Earth to achieve such a temperature is the detonation of a fission bomb. For example, the so-called hydrogen bomb (or H bomb) is actually a deuterium–tritium bomb (a D–T bomb), which uses a nuclear fission reaction to create the very high temperatures needed to initiate fusion of solid lithium deuteride ($^6$LiD), which releases neutrons that then react with $^6$Li, producing tritium. The deuterium-tritium reaction releases energy explosively. Example 9 and its corresponding exercise demonstrate the enormous amounts of energy produced by nuclear fission and fusion reactions. In fact, fusion reactions are the power sources for all stars, including our sun.

## Example 24.5.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when the neutron-induced fission of $^{235}$U produces $^{144}$Cs, $^{90}$Rb, and two neutrons:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + 2{}^{1}_{0}\mathrm{n}$$

**Given:** balanced nuclear reaction

**Asked for:** energy released in electronvolts per atom and kilojoules per mole

**Strategy:**

**A** Following the method used in Example 24.5.1, calculate the change in mass that accompanies the reaction. Convert this value to the change in energy in electronvolts per atom.

**B** Calculate the change in mass per mole of $^{235}$U. Then use Equation 24.5.3 to calculate the change in energy in kilojoules per mole.

**Solution**

**A** The change in mass that accompanies the reaction is as follows:

$$\Delta m = \mathrm{mass}_{\mathrm{products}} - \mathrm{mass}_{\mathrm{reactants}} = \mathrm{mass}({}^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + {}^{1}_{0}\mathrm{n}) - \mathrm{mass}\ {}^{235}_{92}\mathrm{U} \quad (24.5.24)$$

$$= (143.932077\ \mathrm{amu} + 89.914802\ \mathrm{amu} + 1.008665\ \mathrm{amu}) - 235.043930\ \mathrm{amu} \quad (24.5.25)$$

$$= -0.188386\ \mathrm{amu} \quad (24.5.26)$$

The change in energy in electronvolts per atom is as follows:

$$\Delta E = (-0.188386\ \mathrm{amu})(931\ \mathrm{MeV/amu}) = -175\ \mathrm{MeV}$$

**B** The change in mass per mole of $^{235}_{92}$U is −0.188386 g = $-1.88386 \times 10^{-4}$ kg, so the change in energy in kilojoules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.88386 \times 10^{-4}\ \mathrm{kg})(2.998 \times 10^8\ \mathrm{m/s})^2 \quad (24.5.27)$$

$$= -1.693 \times 10^{13}\ \mathrm{J/mol} = -1.693 \times 10^{10}\ \mathrm{kJ/mol} \quad (24.5.28)$$

## Exercise 24.5.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when deuterium and tritium fuse to give helium-4 and a neutron:

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

**Answer**

$\Delta E = -17.6$ MeV/atom $= -1.697 \times 10^{9}$ kJ/mol

## Summary

Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation. Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of $^{1}$H, the experimentally determined mass of an atom is always less than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the mass defect of the nucleus. The energy corresponding to the mass defect is the nuclear binding energy, the amount of energy released when a nucleus forms from its component particles. In nuclear fission, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The critical mass is the minimum mass required to support a self-sustaining nuclear chain reaction. Nuclear fusion is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

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# 24.6: Applied Nuclear Chemistry

**Learning Objectives**

- To understand how nuclear reactors function.

The ever-increasing energy needs of modern societies have led scientists and engineers to develop ways of harnessing the energy released by nuclear reactions. To date, all practical applications of nuclear power have been based on nuclear fission reactions. Although nuclear fusion offers many advantages in principle, technical difficulties in achieving the high energies required to initiate nuclear fusion reactions have thus far precluded using fusion for the controlled release of energy. In this section, we describe the various types of nuclear power plants that currently generate electricity from nuclear reactions, along with some possible ways to harness fusion energy in the future. In addition, we discuss some of the applications of nuclear radiation and radioisotopes, which have innumerable uses in medicine, biology, chemistry, and industry.



Figure 24.6.1: Pitchblende. Pitchblende, the major uranium ore, consisting mainly of uranium oxide.

## Nuclear Reactors

When a critical mass of a fissile isotope is achieved, the resulting flux of neutrons can lead to a self-sustaining reaction. A variety of techniques can be used to control the flow of neutrons from such a reaction, which allows nuclear fission reactions to be maintained at safe levels. Many levels of control are required, along with a fail-safe design, because otherwise the chain reaction can accelerate so rapidly that it releases enough heat to melt or vaporize the fuel and the container, a situation that can release enough radiation to contaminate the surrounding area. Uncontrolled nuclear fission reactions are relatively rare, but they have occurred at least 18 times in the past. The most recent event resulted from the damaged Fukushima Dai-ichi plant after the March 11, 2011, earthquake and tsunami that devastated Japan. The plant used fresh water for cooling nuclear fuel rods to maintain controlled, sustainable nuclear fission. When the water supply was disrupted, so much heat was generated that a partial meltdown occurred. Radioactive iodine levels in contaminated seawater from the plant were over 4300 times the regulated safety limit. To put this in perspective, drinking one liter of fresh water with this level of contamination is the equivalent to receiving double the annual dose of radiation that is typical for a person. Dismantling the plant and decontaminating the site is estimated to require 30 years at a cost of approximately $12 billion.

There is compelling evidence that uncontrolled nuclear chain reactions occurred naturally in the early history of our planet, about 1.7 billion years ago in uranium deposits near Oklo in Gabon, West Africa (Figure 24.6.1). The natural abundance of $^{235}U$ 2 billion years ago was about 3%, compared with 0.72% today; in contrast, the “fossil nuclear reactor” deposits in Gabon now contain only 0.44% $^{235}U$. An unusual combination of geologic phenomena in this region apparently resulted in the formation of deposits of essentially pure uranium oxide containing 3% $^{235}U$, which coincidentally is identical to the fuel used in many modern nuclear plants. When rainwater or groundwater saturated one of these deposits, the water acted as a natural moderator that decreased the kinetic energy of the neutrons emitted by radioactive decay of $^{235}U$, allowing the neutrons to initiate a chain reaction. As a result, the entire deposit “went critical” and became an uncontrolled nuclear chain reaction, which is estimated to have produced about 100 kW of power. It is thought that these natural nuclear reactors operated only intermittently, however, because the heat released would have vaporized the water. Removing the water would have shut down the reactor until the rocks cooled enough to allow water to reenter the deposit, at which point the chain reaction would begin again. This on–off cycle is believed to have been repeated for more than 100,000 years, until so much $^{235}U$ was consumed that the deposits could no longer support a chain reaction.



Figure 24.6.1: A “Fossil Nuclear Reactor” in a Uranium Mine Near Oklo in Gabon, West Africa. More than a billion years ago, a number of uranium-rich deposits in West Africa apparently “went critical,” initiating uncontrolled nuclear fission reactions that may have continued intermittently for more than 100,000 years, until the concentration of uranium-235 became too low to support a chain reaction. This photo shows a geologist standing in a mine dug to extract the concentrated uranium ore. Commercial interest waned rapidly after it was recognized that the uranium ore was severely depleted in uranium-235, the isotope of interest.

In addition to the incident in Japan, another recent instance of an uncontrolled nuclear chain reaction occurred on April 25–26, 1986, at the Chernobyl nuclear power plant in the former Union of Soviet Socialist Republics (USSR; now in the Ukraine; Figure 24.6.2). During testing of the reactor’s turbine generator, a series of mechanical and operational failures caused a chain reaction that quickly went out of control, destroying the reactor core and igniting a fire that destroyed much of the facility and released a large amount of radioactivity. Thirty people were killed immediately, and the high levels of radiation in a 20 mi radius forced nearly 350,000 people to be resettled or evacuated. In addition, the accident caused a disruption to the Soviet economy that is estimated to have cost almost $13 billion. It is somewhat surprising, however, that the long-term health effects on the 600,000 people affected by the accident appear to be much less severe than originally anticipated. Initially, it was predicted that the accident would result in tens of thousands of premature deaths, but an exhaustive study almost 20 yr after the event suggests that 4000 people will die prematurely from radiation exposure due to the accident. Although significant, in fact it represents only about a 3% increase in the cancer rate among the 600,000 people most affected, of whom about a quarter would be expected to eventually die of cancer even if the accident had not occurred.



Figure 24.6.2: The Chernobyl Nuclear Power Plant. In 1986, mechanical and operational failures during testing at the Chernobyl power plant in the USSR (now in the Ukraine) caused an uncontrolled nuclear chain reaction. The resulting fire destroyed much of the facility and severely damaged the core of the reactor, resulting in the release of large amounts of radiation that was spread over the surrounding area by the prevailing winds. The effects were devastating to the health of the population in the region and to the Soviet economy.

If, on the other hand, the neutron flow in a reactor is carefully regulated so that only enough heat is released to boil water, then the resulting steam can be used to produce electricity. Thus a nuclear reactor is similar in many respects to the conventional power plants that burn coal or natural gas to generate electricity; the only difference is the source of the heat that converts water to steam.

## Light-Water Reactors

We begin our description of nuclear power plants with light-water reactors, which are used extensively to produce electricity in countries such as Japan, Israel, South Korea, Taiwan, and France—countries that lack large reserves of fossil fuels. The essential components of a light-water reactor are depicted in Figure 24.6.3. All existing nuclear power plants have similar components, although different designs use different fuels and operating conditions. Fuel rods containing a fissile isotope in a structurally stabilized form (such as uranium oxide pellets encased in a corrosion-resistant zirconium alloy) are suspended in a cooling bath that transfers the heat generated by the fission reaction to a secondary cooling system. The heat is used to generate steam for the production of electricity. In addition, control rods are used to absorb neutrons and thereby control the rate of the nuclear chain reaction. Control rods are made of a substance that efficiently absorbs neutrons, such as boron, cadmium, or, in nuclear submarines, hafnium. Pulling the control rods out increases the neutron flux, allowing the reactor to generate more heat, whereas inserting the rods completely stops the reaction, a process called “scramming the reactor.”

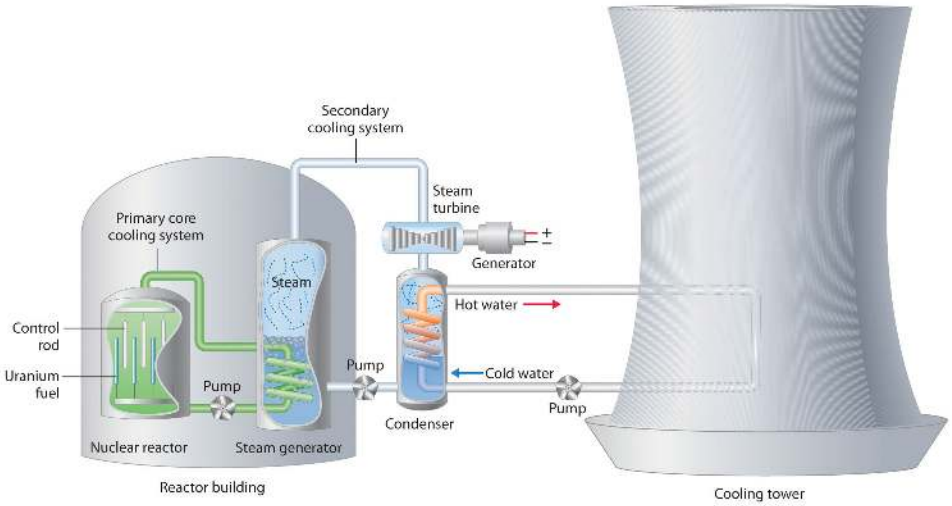



Figure 24.6.3: A Light-Water Nuclear Fission Reactor for the Production of Electric Power. The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of $^{235}U$ in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium, which are very effective at absorbing neutrons, are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

Despite this apparent simplicity, many technical hurdles must be overcome for nuclear power to be an efficient and safe source of energy. Uranium contains only 0.72% uranium-235, which is the only naturally occurring fissile isotope of uranium. Because this abundance is not enough to support a chain reaction, the uranium fuel must be at least partially enriched in $^{235}U$, to a concentration of about 3%, for it to be able to sustain a chain reaction. At this level of enrichment, a nuclear explosion is impossible; far higher levels of enrichment (greater than or equal to 90%) are required for military applications such as nuclear weapons or the nuclear reactors in submarines. Enrichment is accomplished by converting uranium oxide to $UF_6$, which is volatile and contains discrete $UF_6$ molecules. Because $^{235}UF_6$ and $^{238}UF_6$ have different masses, they have different rates of effusion and diffusion, and they can be separated using a gas diffusion process. Another difficulty is that neutrons produced by nuclear fission are too energetic to be absorbed by neighboring nuclei, and they escape from the material without inducing fission in nearby $^{235}U$ nuclei. Consequently, a moderator must be used to slow the neutrons enough to allow them to be captured by other $^{235}U$ nuclei. High-speed neutrons are scattered by substances such as water or graphite, which decreases their kinetic energy and increases the probability that they will react with another $^{235}U$ nucleus. The moderator in a light-water reactor is the water that is used as the primary coolant. The system is highly pressurized to about 100 atm to keep the water from boiling at 100°C.

All nuclear reactors require a powerful cooling system to absorb the heat generated in the reactor core and create steam that is used to drive a turbine that generates electricity. In 1979, an accident occurred when the main water pumps used for cooling at the nuclear power plant at Three Mile Island in Pennsylvania stopped running, which prevented the steam generators from removing heat. Eventually, the zirconium casing of the fuel rods ruptured, resulting in a meltdown of about half of the reactor core. Although there was no loss of life and only a small release of radioactivity, the accident produced sweeping changes in nuclear power plant operations. The US Nuclear Regulatory Commission tightened its oversight to improve safety.

The main disadvantage of nuclear fission reactors is that the spent fuel, which contains too little of the fissile isotope for power generation, is much more radioactive than the unused fuel due to the presence of many daughter nuclei with shorter half-lives than $^{235}U$. The decay of these daughter isotopes generates so much heat that the spent fuel rods must be stored in water for as long as 5 yr before they can be handled. Even then, the radiation levels are so high that the rods must be stored for many, many more years to allow the daughter isotopes to decay to nonhazardous levels. How to store these spent fuel rods for hundreds of years is a pressing issue that has not yet been successfully resolved. As a result, some people are convinced that nuclear power is not a viable option for providing our future energy needs, although a number of other countries continue to rely on nuclear reactors for a large fraction of their energy.

## Heavy-Water Reactors

Deuterium ($^2$H) absorbs neutrons much less effectively than does hydrogen ($^1$H), but it is about twice as effective at slowing neutrons. Consequently, a nuclear reactor that uses $D_2O$ instead of $H_2O$ as the moderator is so efficient that it can use unenriched uranium as fuel. Using a lower grade of uranium reduces operating costs and eliminates the need for plants that produce enriched uranium. Because of the expense of $D_2O$, however, only countries like Canada, which has abundant supplies of hydroelectric power for generating $D_2O$ by electrolysis, have made a major investment in heavy-water reactors.

## Breeder Reactors

A breeder reactor is a nuclear fission reactor that produces more fissionable fuel than it consumes. This does not violate the first law of thermodynamics because the fuel produced is not the same as the fuel consumed. Under heavy neutron bombardment, the nonfissile $^{238}$U isotope is converted to $^{239}$Pu, which can undergo fission:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta \tag{24.6.1}$$

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta \tag{24.6.2}$$

The overall reaction is thus the conversion of nonfissile $^{238}$U to fissile $^{239}$Pu, which can be chemically isolated and used to fuel a new reactor. An analogous series of reactions converts nonfissile $^{232}$Th to $^{233}$U, which can also be used as a fuel for a nuclear reactor. Typically, about 8–10 yr are required for a breeder reactor to produce twice as much fissile material as it consumes, which is enough to fuel a replacement for the original reactor plus a new reactor. The products of the fission of $^{239}$Pu, however, have substantially longer half-lives than the fission products formed in light-water reactors.

## Nuclear Fusion Reactors

Although nuclear fusion reactions, are thermodynamically spontaneous, the positive charge on both nuclei results in a large electrostatic energy barrier to the reaction (remember that thermodynamic spontaneity is unrelated to the reaction rate.) Extraordinarily high temperatures (about $1.0 \times 10^8$°C) are required to overcome electrostatic repulsions and initiate a fusion reaction. Even the most feasible such reaction, deuterium–tritium fusion (D–T fusion), requires a temperature of about $4.0 \times 10^7$°C. Achieving these temperatures and controlling the materials to be fused are extraordinarily difficult problems, as is extracting the energy released by the fusion reaction, because a commercial fusion reactor would require such high temperatures to be maintained for long periods of time. Several different technologies are currently being explored, including the use of intense magnetic fields to contain ions in the form of a dense, high-energy plasma at a temperature high enough to sustain fusion (Figure 24.6.4*a*). Another concept employs focused laser beams to heat and compress fuel pellets in controlled miniature fusion explosions (Figure 24.6.4*b*).

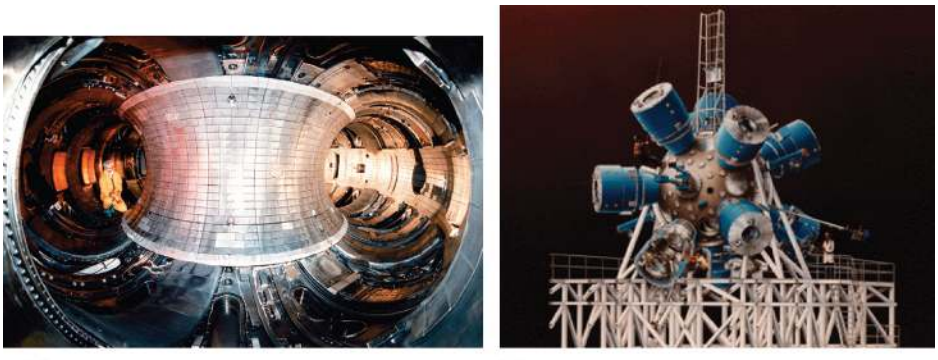



Figure 24.6.4: Two Possible Designs for a Nuclear Fusion Reactor. The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. (a) One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. Because plasma is essentially a gas composed of ionized particles, it can be confined using a strong magnetic field shaped like a torus (a hollow donut). (b) Another approach to nuclear fusion is inertial confinement, which uses an icosahedral array of powerful lasers to heat and compress a tiny fuel pellet (a mixture of solid LiD and LiT) to induce fusion.

Nuclear reactions such as these are called **thermonuclear reactions** because a great deal of thermal energy must be invested to initiate the reaction. The amount of energy released by the reaction, however, is several orders of magnitude greater than the energy needed to initiate it. In principle, a nuclear fusion reaction should thus result in a significant net production of energy. In addition,

Earth's oceans contain an essentially inexhaustible supply of both deuterium and tritium, which suggests that nuclear fusion could provide a limitless supply of energy. Unfortunately, however, the technical requirements for a successful nuclear fusion reaction are so great that net power generation by controlled fusion has yet to be achieved.

## The Uses of Radioisotopes

Nuclear radiation can damage biological molecules, thereby disrupting normal functions such as cell division. Because radiation is particularly destructive to rapidly dividing cells such as tumor cells and bacteria, it has been used medically to treat cancer since 1904, when radium-226 was first used to treat a cancerous tumor. Many radioisotopes are now available for medical use, and each has specific advantages for certain applications.

In modern radiation therapy, radiation is often delivered by a source planted inside the body. For example, tiny capsules containing an isotope such as $^{192}$Ir, coated with a thin layer of chemically inert platinum, are inserted into the middle of a tumor that cannot be removed surgically. The capsules are removed when the treatment is over. In some cases, physicians take advantage of the body's own chemistry to deliver a radioisotope to the desired location. For example, the thyroid glands in the lower front of the neck are the only organs in the body that use iodine. Consequently, radioactive iodine is taken up almost exclusively by the thyroid (Figure 24.6.5$a$). Thus when radioactive isotopes of iodine ($^{125}$I or $^{131}$I) are injected into the blood of a patient suffering from thyroid cancer, the thyroid glands filter the radioisotope from the blood and concentrate it in the tissue to be destroyed. In cases where a tumor is surgically inaccessible (e.g., when it is located deep in the brain), an external radiation source such as a $^{60}$Co "gun" is used to aim a tightly focused beam of γ rays at it. Unfortunately, radiation therapy damages healthy tissue in addition to the target tumor and results in severe side effects, such as nausea, hair loss, and a weakened immune system. Although radiation therapy is generally not a pleasant experience, in many cases it is the only choice.

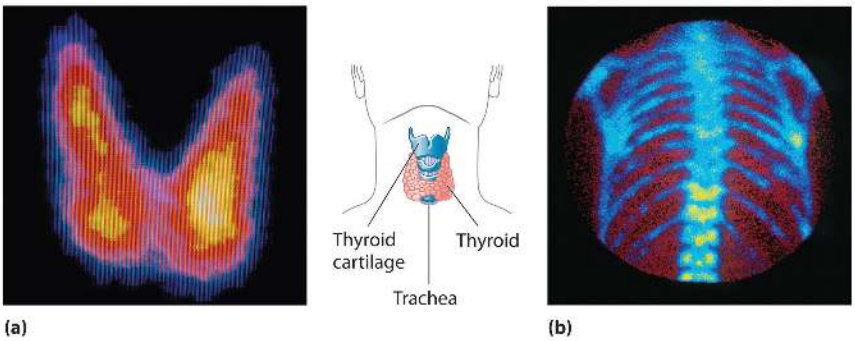



Figure 24.6.5: Medical Imaging and Treatment with Radioisotopes. (a) Radioactive iodine is used both to obtain images of the thyroid and to treat thyroid cancer. Injected iodine-123 or iodine-131 is selectively taken up by the thyroid gland, where it is incorporated into the thyroid hormone: thyroxine. Because iodine-131 emits low-energy β particles that are absorbed by the surrounding tissue, it can be used to destroy malignant tissue in the thyroid. In contrast, iodine-123 emits higher-energy γ rays that penetrate tissues readily, enabling it to image the thyroid gland, as shown here. (b) Some technetium compounds are selectively absorbed by cancerous cells within bones. The yellow spots show that a primary cancer has metastasized (spread) to the patient's spine (lower center) and ribs (right center).

A second major medical use of radioisotopes is medical imaging, in which a radioisotope is temporarily localized in a particular tissue or organ, where its emissions provide a "map" of the tissue or the organ. Medical imaging uses radioisotopes that cause little or no tissue damage but are easily detected. One of the most important radioisotopes for medical imaging is $^{99m}$Tc. Depending on the particular chemical form in which it is administered, technetium tends to localize in bones and soft tissues, such as the heart or the kidneys, which are almost invisible in conventional x-rays (Figure 24.6.5$b$). Some properties of other radioisotopes used for medical imaging are listed in Table 24.6.1.

Table 24.6.1: Radioisotopes Used in Medical Imaging and Treatment

| Isotope | Half-Life | Tissue |
|---|---|---|
| $^{18}F$ | 110 min | brain |
| $^{24}Na$ | 15 h | circulatory system |
| $^{32}P$ | 14 days | eyes, liver, and tumors |
| $^{59}Fe$ | 45 days | blood and spleen |
| $^{60}Co$ | 5.3 yr | external radiotherapy |
| $^{99m}Tc$ | 6 h | heart, thyroid, liver, kidney, lungs, and skeleton |
| $^{125}I$ | 59.4 days | thyroid, prostate, and brain |
| $^{131}I$ | 8 days | thyroid |
| $^{133}Xe$ | 5 days | lungs |
| $^{201}Tl$ | 3 days | heart |

Because γ rays produced by isotopes such as $^{131}I$ and $^{99m}Tc$ are emitted randomly in all directions, it is impossible to achieve high levels of resolution in images that use such isotopes. However, remarkably detailed three-dimensional images can be obtained using an imaging technique called positron emission tomography (PET). The technique uses radioisotopes that decay by positron emission, and the resulting positron is annihilated when it collides with an electron in the surrounding matter. In the annihilation process, both particles are converted to energy in the form of two γ rays that are emitted simultaneously and at 180° to each other:

$$^{0}_{+1}\beta + {}^{0}_{-1}e \rightarrow 2^{0}_{0}\gamma \tag{24.6.3}$$

With PET, biological molecules that have been "tagged" with a positron-emitting isotope such as $^{18}F$ or $^{11}C$ can be used to probe the functions of organs such as the brain.

Another major health-related use of ionizing radiation is the irradiation of food, an effective way to kill bacteria such as *Salmonella* in chicken and eggs and potentially lethal strains of *Escherichia coli* in beef. Collectively, such organisms cause almost 3 million cases of food poisoning annually in the United States, resulting in hundreds of deaths. Figure 24.6.6 shows how irradiation dramatically extends the storage life of foods such as strawberries. Although US health authorities have given only limited approval of this technique, the growing number of illnesses caused by antibiotic-resistant bacteria is increasing the pressure to expand the scope of food irradiation.




Figure 24.6.6: The Preservation of Strawberries with Ionizing Radiation. Fruits such as strawberries can be irradiated by high-energy γ rays to kill bacteria and prolong their storage life. The nonirradiated strawberries on the left are completely spoiled after 15 days in storage, but the irradiated strawberries on the right show no visible signs of spoilage under the same conditions.

One of the more unusual effects of radioisotopes is in dentistry. Because dental enamels contain a mineral called feldspar ($KAlSi_3O_8$, which is also found in granite rocks), teeth contain a small amount of naturally occurring radioactive $^{40}K$. The radiation caused by the decay of $^{40}K$ results in the emission of light (fluorescence), which gives the highly desired “pearly white” appearance associated with healthy teeth.

In a sign of how important nuclear medicine has become in diagnosing and treating illnesses, the medical community has become alarmed at the global shortage of $^{99}Tc$, a radioisotope used in more than 30 million procedures a year worldwide. Two reactors that produce 60% of the world’s radioactive $^{99}Mo$, which decays to $^{99}Tc$, are operating beyond their intended life expectancies. Moreover, because most of the reactors producing $^{99}Mo$ use weapons-grade uranium ($^{235}U$), which decays to 99Mo during fission, governments are working to phase out civilian uses of technology to produce $^{99}Mo$ because of concerns that the technology can be used to produce nuclear weapons. Engineers are currently focused on how to make key medical isotopes with other alternatives that don’t require fission. One promising option is by removing a neutron from $^{100}Mo$, a stable isotope that makes up about 10% of natural molybdenum, transmuting it to $^{99}Mo$.

In addition to the medical uses of radioisotopes, radioisotopes have literally hundreds of other uses. For example, smoke detectors contain a tiny amount of $^{241}Am$, which ionizes the air in the detector so an electric current can flow through it. Smoke particles reduce the number of ionized particles and decrease the electric current, which triggers an alarm. Another application is the “go-devil” used to detect leaks in long pipelines. It is a packaged radiation detector that is inserted into a pipeline and propelled through the pipe by the flowing liquid. Sources of $^{60}Co$ are attached to the pipe at regular intervals; as the detector travels along the pipeline, it sends a radio signal each time it passes a source. When a massive leak causes the go-devil to stop, the repair crews know immediately which section of the pipeline is damaged. Finally, radioactive substances are used in gauges that measure and control the thickness of sheets and films. As shown in Figure 24.6.7, thickness gauges rely on the absorption of either β particles (by paper, plastic, and very thin metal foils) or γ rays (for thicker metal sheets); the amount of radiation absorbed can be measured accurately and is directly proportional to the thickness of the material.

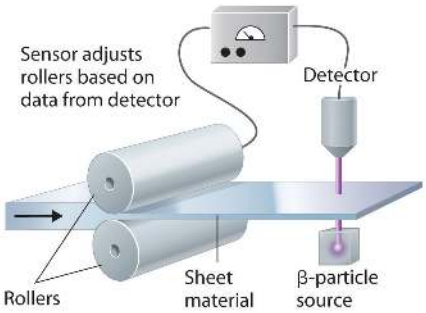



Figure 24.6.7: Using Radiation to Control the Thickness of a Material. Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material being produced and a detector on the other. An increase in the amount of radiation that reaches the detector indicates a decrease in the thickness of the material and vice versa. The output of the detector can thus be used to control the thickness of the material.

## Summary

All practical applications of nuclear power have been based on nuclear fission reactions, which nuclear power plants use to generate electricity. In nuclear power plants, nuclear reactions generate electricity. Light-water reactors use enriched uranium as a fuel. They include fuel rods, a moderator, control rods, and a powerful cooling system to absorb the heat generated in the reactor core. Heavy-water reactors use unenriched uranium as a fuel because they use $D_2O$ as the moderator, which scatters and slows neutrons much more effectively than $H_2O$. A breeder reactor produces more fissionable fuel than it consumes. A nuclear fusion reactor requires very high temperatures. Fusion reactions are thermonuclear reactions because they require high temperatures for initiation. Radioisotopes are used in both radiation therapy and medical imaging.

# Contributors

- Anonymous

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# 24.7: The Origin of the Elements

**Learning Objectives**

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the $^{56}Fe$ nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen ($^{1}H$), which accounts for about 90% of all atoms. In fact, $^{1}H$ is the raw material from which all other elements are formed.

In this section, we explain why $^{1}H$ and $^{2}He$ together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

## Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure 24.6.1. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure 24.6.1 illustrate two important points. First, except for hydrogen, the most abundant elements have *even* atomic numbers. Not only is this consistent with the trends in nuclear stability discussed in Section 24.1, but it also suggests that heavier elements are formed by combining helium nuclei ($Z = 2$). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table 24.6.1 for some common elements. Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as $NH_3$, $CH_4$, and $H_2O$. Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as $^{40}K$. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much *less* abundant on Earth than in the universe; some examples are Ru and Ir. You may recall from Chapter 1 that the anomalously high iridium content of a 66-million-year-old rock layer was a key finding in the development of the asteroid-impact theory for the extinction of the dinosaurs. This section explains some of the reasons for the great differences in abundances of the metallic elements.

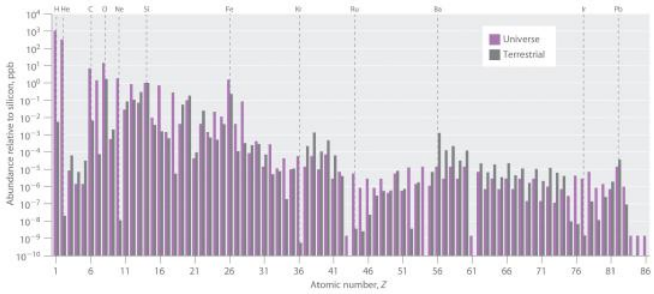



Figure **24.6.1 The Relative Abundances of the Elements in the Universe and on Earth** In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are *very* different from their relative abundances on Earth.

**Table 24.6.1 Relative Abundances of Elements on Earth and in the Known Universe**


https://chem.libretexts.org/@go/page/349817

| Terrestrial/Universal Element | Abundance Ratio |
|---|---|
| H | 0.0020 |
| He | $2.4 \times 10^{-8}$ |
| C | 0.36 |
| N | 0.02 |
| O | 46 |
| Ne | $1.9 \times 10^{-6}$ |
| Na | 1200 |
| Mg | 48 |
| Al | 1600 |
| Si | 390 |
| S | 0.84 |
| K | 5000 |
| Ca | 710 |
| Ti | 2200 |
| Fe | 57 |

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

## Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure 24.6.2). Initially, all stars are formed by the aggregation of interstellar "dust," which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm$^3$, and the temperature increases to about $1.5 \times 10^7$ K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star "ignites," creating a *yellow star* like our sun.

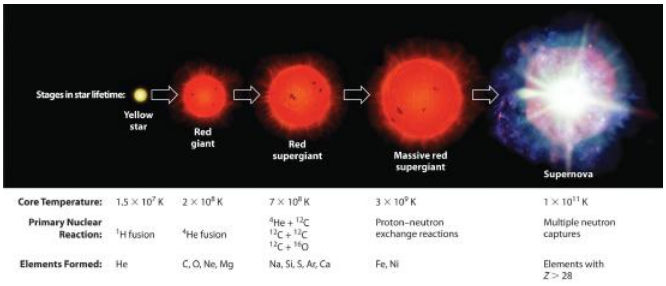



Figure 24.6.2 Nuclear Reactions during the Life Cycle of a Massive Star At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

$$^{1}_{1}H + \ ^{1}_{1}H \rightarrow \ ^{2}_{1}H + \ ^{0}_{+1}\beta$$

$$^{2}_{1}H + ^{1}_{1}H \rightarrow ^{3}_{2}He + ^{0}_{0}\gamma$$

$$^{3}_{2}He + ^{3}_{2}He \rightarrow ^{4}_{2}He + 2^{1}_{1}H$$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

$$4^{1}_{1}H \rightarrow ^{4}_{2}He + 2_{+1}{}^{0}\beta + 2^{0}_{0}\gamma$$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about $2 \times 10^8$ K, the helium-4 nuclei begin to fuse, producing beryllium-8:

$$2^{4}_{2}He \rightarrow ^{8}_{4}Be$$

Although beryllium-8 has both an even mass number and an even atomic number, its also has a low neutron-to-proton ratio (and other factors beyond the scope of this text) that makes it unstable; it decomposes in only about $10^{-16}$ s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

$$^{8}_{4}Be \xrightarrow{^{4}_{2}He} \ ^{12}_{6}C \xrightarrow{^{4}_{2}He} \ ^{16}_{8}O \xrightarrow{^{4}_{2}He} \ ^{20}_{10}Ne \xrightarrow{^{4}_{2}He} \ ^{24}_{12}Mg$$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a *red giant* that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm$^3$, so the core becomes even hotter. At a temperature of about $7 \times 10^8$ K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

$$^{12}_{6}C + \ ^{12}_{6}C \rightarrow \ ^{23}_{11}Na + \ ^{1}_{1}H$$

$$^{12}_{6}C + \ ^{16}_{8}O \rightarrow \ ^{28}_{14}Si + \ ^{0}_{0}\gamma$$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

$$^{12}_{6}C \xrightarrow{^{4}_{2}He} \ ^{16}_{8}O \xrightarrow{^{4}_{2}He} \ ^{20}_{10}Ne \xrightarrow{^{4}_{2}He} \ ^{24}_{12}Mg \xrightarrow{^{4}_{2}He} \ ^{28}_{14}Si \xrightarrow{^{4}_{2}He} \ ^{32}_{16}S \xrightarrow{^{4}_{2}He} \ ^{36}_{18}Ar \xrightarrow{^{4}_{2}He} \ ^{40}_{20}Ca$$

The energy released by these reactions causes a further expansion of the star to form a *red supergiant*, and the core temperature increases steadily. At a temperature of about $3 \times 10^9$ K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

## The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with $Z > 28$. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called *supernovas* (Figure 24.6.2). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting *neutron star* is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or *nebula* (Figure 24.6.3). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

$$^{56}_{26}Fe + \ 64^{1}_{0}n \rightarrow \ ^{120}_{26}Fe \rightarrow \ ^{120}_{50}Sn + 24_{-1}{}^{0}\beta$$



**Figure 24.6.3 A Supernova** A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

## Example 24.6.1

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

1. magnesium-24.
2. neon-20 from two carbon-12 nuclei.

**Given:** reactant and product nuclides

**Asked for:** balanced nuclear equation

**Strategy:**

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

**Solution:**

1. A magnesium-24 nucleus ($Z$ = 12, $A$ = 24) has the same nucleons as two carbon-12 nuclei ($Z$ = 6, $A$ = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: ${}^{12}_{6}C + {}^{12}_{6}C \rightarrow {}^{24}_{12}Mg$
2. The neon-20 product has $Z$ = 10 and $A$ = 20. The conservation of mass requires that the other product have $A = (2 \times 12) - 20 = 4$; because of conservation of charge, it must have $Z = (2 \times 6) - 10 = 2$. These are the characteristics of an α particle. The reaction is therefore ${}^{12}_{6}C + {}^{12}_{6}C \rightarrow {}^{20}_{10}Ne + {}^{4}_{2}\alpha$

Exercise

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

**Answer:** 19 neutrons; ${}^{56}_{26}Fe + 19{}^{1}_{0}n \rightarrow {}^{75}_{26}Fe \rightarrow {}^{75}_{33}As + 7\,{}^{0}_{-1}\beta$

## Summary

By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

## Key Takeaways

- Hydrogen and helium are the most abundant elements in the universe.
- Heavier elements are formed in the interior of stars via multiple neutron-capture events.

## Conceptual Problems

1. Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?
2. How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?
3. Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.
4. During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star "lit." Explain the different reactions that dominate in the different stages of a star's life cycle and their effect on the temperature of the star.
5. A line in a popular song from the 1960s by Joni Mitchell stated, "We are stardust…." Does this statement have any merit or is it just poetic? Justify your answer.
6. If the laws of physics were different and the primary element in the universe were boron-11 ($Z = 5$), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

## Answer

1.
2.
3. The raw material for all elements with $Z > 2$ is helium ($Z = 2$), and fusion of helium nuclei will always produce nuclei with an even number of protons.
4.
5.
6.

## Numerical Problems

1. Write a balanced nuclear reaction for the formation of each isotope.
    1. $^{27}$Al from two $^{12}$C nuclei
    2. $^{9}$Be from two $^{4}$He nuclei
2. At the end of a star's life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.
    1. $^{106}$Pd from nickel-58
    2. selenium-79 from iron-56
3. When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be "burned" in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

## Contributors

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# 24.E: Nuclear Chemistry (Exercises)

A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: Principles, Patterns, and Applications**

by Bruce A. Averill



Template:HideTOC

These are homework exercises to accompany the Textmap created for "Chemistry: Principles, Patterns, and Applications" by Bruce A. Averill and Patricia Eldredge. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

## 20.1: Components of the Nucleus

### Conceptual Problems

1. What distinguishes a nuclear reaction from a chemical reaction? Use an example of each to illustrate the differences.

2. What do chemists mean when they say a substance is *radioactive*?

3. What characterizes an isotope? How is the mass of an isotope of an element related to the atomic mass of the element shown in the periodic table?

4. In a typical nucleus, why does electrostatic repulsion between protons not destabilize the nucleus? How does the neutron-to-proton ratio affect the stability of an isotope? Why are all isotopes with $Z > 83$ unstable?

5. What is the significance of a *magic number* of protons or neutrons? What is the relationship between the number of stable isotopes of an element and whether the element has a magic number of protons?

6. Do you expect Bi to have a large number of stable isotopes? Ca? Explain your answers.

7. Potassium has three common isotopes, $^{39}$K, $^{40}$K, and $^{41}$K, but only potassium-40 is radioactive (a beta emitter). Suggest a reason for the instability of $^{40}$K.

8. Samarium has 11 relatively stable isotopes, but only 4 are nonradioactive. One of these 4 isotopes is $^{144}$Sm, which has a lower neutron-to-proton ratio than lighter, radioactive isotopes of samarium. Why is $^{144}$Sm more stable?

### Answers

5. Isotopes with magic numbers of protons and/or neutrons tend to be especially stable. Elements with magic numbers of protons tend to have more stable isotopes than elements that do not.

7. Potassium-40 has 19 protons and 21 neutrons. Nuclei with odd numbers of both protons and neutrons tend to be unstable. In addition, the neutron-to-proton ratio is very low for an element with this mass, which decreases nuclear stability.

### Numerical Problems

1. Write the nuclear symbol for each isotope using ${}^{A}_{Z}\mathrm{X}$ notation.

   a. chlorine-39

   b. lithium-8

   c. osmium-183

   d. zinc-71

2.Write the nuclear symbol for each isotope using ${}^{A}_{Z}\mathrm{X}$ notation.

a. lead-212

b. helium-5

c. oxygen-19

d. plutonium-242

3. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

a. iron-57

b. ${}^{185}\mathrm{W}$

c. potassium-39

d. ${}^{131}\mathrm{Xe}$

4. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.

a. technetium-99*m*

b. ${}^{140}\mathrm{La}$

c. radium-227

d. ${}^{208}\mathrm{Bi}$

5. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

a. ${}^{20}\mathrm{Ne}$

b. tungsten-184

c. ${}^{106}\mathrm{Ti}$

6. Which of these nuclides do you expect to be radioactive? Explain your reasoning.

a. ${}^{107}\mathrm{Ag}$

b. ${}^{50}\mathrm{V}$

c. lutetium-176

### Answers

1.

a. ${}^{39}_{17}\mathrm{Cl}$

b. ${}^{8}_{3}\mathrm{Li}$

c. ${}^{183}_{76}\mathrm{Os}$

d. ${}^{71}_{30}\mathrm{Zn}$

3.

a. 26 protons; 31 neutrons; 1.19

b. 74 protons; 111 neutrons; 1.50

c. 19 protons; 20 neutrons; 1.05

d. 54 protons; 77 neutrons; 1.43

## 20.2: Nuclear Reactions

## Conceptual Problems

1. Describe the six classifications of nuclear decay reactions. What is the most common mode of decay for elements that have heavy nuclei? Why?
2. Complete the following table for these five nuclear reactions.

| | Alpha Decay | Beta Decay | Gamma Emission | Positron Emission | Electron Capture |
|---|---|---|---|---|---|
| identity of particle or radiation | helium-4 nucleus | | | | |
| mass number of parent − mass number of daughter | 4 | | | | |
| atomic number of parent − atomic number of daughter | | −1 | | | |
| effect on neutron-to-proton ratio | | decreases | | | |

3. What is the most common decay process for elements in row 5 of the periodic table that contain too few neutrons for the number of protons present? Why?
4. Explain the difference between the symbols $e^-$ and $\beta^-$. What is the difference in meaning between the symbols $^4_2\text{He}$ and $^4_2\alpha$?
5. What is a mass number? Which particles have a mass number of zero?
6. What are the key differences between the equations written for chemical reactions and for nuclear reactions? How are they similar?
7. Can all the kinds of nuclear decay reactions discussed be characterized by the general equation: parent → daughter + particle? Explain your answer.
8. Which types of nuclear decay reactions conserve both mass number and atomic number? In which do the parent and daughter nuclei have the same mass number but different atomic numbers? Which do not convert one element to another?
9. Describe a radioactive decay series. How many series occur naturally? Of these, which one no longer occurs in nature? Why?
10. Primordial nuclides are nuclides found on Earth that have existed in their current form since before Earth was formed. Primordial nuclides are residues from the Big Bang, from cosmogenic sources, and from ancient supernova explosions which occurred before the formation of the Solar System. Only four primordial nuclides with atomic numbers greater than lead (Z>82)) still exist ($^{209}$Bi, $^{232}$Th, $^{235}$U, and $^{238}$U) - and all of them are radioactive. Except for some isotopes of thorium and uranium that have a very long half-life, the half-lives of the heavy elements are so short that these elements should have been completely converted to lighter, more stable elements long ago. Why are these elements still present in nature?
11. Why are neutrons preferred to protons when preparing new isotopes of the lighter elements?
12. Why are particle accelerators and cyclotrons needed to create the transuranium elements?

## Answers

3. Both positron decay and electron capture increase the neutron-to-proton ratio; electron capture is more common for heavier elements such those of row 5.
5. The mass number is the sum of the numbers of protons and neutrons present. Particles with a mass number of zero include β particles (electrons) and positrons; gamma rays and x-rays also have a mass number of zero.
11. Unlike protons, neutrons have no charge, which minimizes the electrostatic barrier to colliding and reacting with a positively charged nucleus.

## Numerical Problems

1. What type of particle is emitted in each nuclear reaction?
   a. $^{238}Pu \rightarrow {}^{234}U$
   b. $^{32}Si \rightarrow {}^{32}P$
   c. $^{18}F \rightarrow {}^{18}O$
   d. $^{206}Tl \rightarrow {}^{206}Pb$

2. What type of particle is emitted in each nuclear reaction?
   a. $^{230}Th \rightarrow {}^{226}Ra$
   b. $^{224}Rn \rightarrow {}^{224}Fr$
   c. $^{210}Bi \rightarrow {}^{206}Tl$
   d. $^{36}Cl \rightarrow {}^{36}S$

3. Predict the mode of decay and write a balanced nuclear reaction for each isotope.
   a. $^{235}U$
   b. $^{254}Es$
   c. $^{36}S$
   d. $^{99}Mo$

4. Predict the mode of decay and write a balanced nuclear reaction for each isotope.
   a. $^{13}N$
   b. $^{231}Pa$
   c. $^{7}Be$
   d. $^{77}Ge$

5. Balance each nuclear reaction.
   a. $^{208}Po \rightarrow \alpha + Pb$
   b. $^{226}Ra \rightarrow \alpha + Rn$
   c. $^{228}Th \rightarrow Ra + \alpha + \gamma$
   d. $^{231}Pa \rightarrow Ac + \alpha + \gamma$
   e. $Ho \rightarrow {}^{166}Er + \beta^- + \gamma$
   f. $Ac \rightarrow {}^{226}Th + \beta^- + \gamma$

6. Complete each nuclear reaction.
   a. $^{210}_{84}Po \rightarrow {}^{206}Pb$
   b. $^{217}_{85}At \rightarrow Bi + \alpha$
   c. $Ra \rightarrow ^{220}_{86}Rn + \alpha$
   d. $^{208}Tl \rightarrow {}^{82}Pb + \beta^-$
   e. $Np \rightarrow {}^{239}Pu + \beta^-$
   f. $Fe \rightarrow {}^{52}Mn + \beta^+ + \gamma$

7. Write a balanced nuclear equation for each reaction.
   a. $\beta^-$ decay of $^{87}Rb$
   b. $\beta^+$ decay of $^{20}Mg$
   c. $\alpha$ decay of $^{268}Mt$

8. Write a balanced nuclear equation for each reaction.
   a. $\beta^-$ decay of $^{45}K$
   b. $\beta^+$ decay of $^{41}Sc$
   c. $\alpha$ decay of $^{146}Sm$

9. The decay products of several isotopes are listed here. Identify the type of radiation emitted and write a balanced nuclear equation for each.

a. $^{218}Po \rightarrow {}^{214}Pb$
b. $^{32}Si \rightarrow {}^{32}P$
c. an excited state of an iron-57 nucleus decaying to its ground state
d. conversion of thallium-204 to lead-204

10. The decay products of several isotopes are listed here. Identify the type of radiation emitted and write a balanced nuclear equation for each.
    a. $^{218}Po \rightarrow {}^{218}At$
    b. $^{216}Po \rightarrow {}^{212}Pb$
    c. bismuth-211 converted to thallium-207
    d. americium-242 converted to rhodium-107 with the emission of four neutrons
11. Predict the most likely mode of decay and write a balanced nuclear reaction for each isotope.
    a. $^{238}U$
    b. $^{208}Po$
    c. $^{40}S$
    d. molybdenum-93m
12. Predict the most likely mode of decay and write a balanced nuclear reaction for each isotope.
    a. $^{16}N$
    b. $^{224}Th$
    c. $^{118}In$
    d. $^{64}Ge$
13. For each nuclear reaction, identify the type(s) of decay and write a balanced nuclear equation.
    a. $^{216}Po \rightarrow ? + At$
    b. $? \rightarrow \alpha + {}^{231}Pa$
    c. $^{228}Th \rightarrow ? + \alpha + \gamma$
    d. $^{231}Pa \rightarrow ? + \beta^{-} + \gamma$
14. For each nuclear reaction, identify the type(s) of decay and write a balanced nuclear equation.
    a. $^{212}Po \rightarrow {}^{208}Pb + ?$
    b. $^{192}Ir \rightarrow Pt + ?$
    c. $^{241}Am \rightarrow {}^{57}Fe + {}^{184}? + ?$
    d. $Ge \rightarrow {}^{77}Ge + ?$
15. Identify the parent isotope and write a balanced nuclear reaction for each process.
    a. Lead-205 is formed via an alpha emission.
    b. Titanium-46 is formed via beta and gamma emission.
    c. Argon-36 is formed via a beta decay and a gamma emission.
16. Identify the parent isotope and write a balanced nuclear reaction for each process.
    a. Iodine-130 is formed by ejecting an electron and a gamma ray from a nucleus.
    b. Uranium-240 is formed by alpha decay.
    c. Curium-247 is formed by releasing a helium dication and a gamma ray.
17. Write a balanced nuclear equation for each process.
    a. Bromine undergoes a decay and produces a gas with an atomic mass of 80 amu.
    b. An element emits two neutrons while decaying into two metals, each of which can be extracted and converted to chlorides with the formula $MCl_2$. The masses of the two salts are 162.9 and 210.9 g/mol, respectively.
18. Write a balanced nuclear equation for each process.
    a. An unknown element emits γ rays plus particles that are readily blocked by paper. The sample also contains a substantial quantity of tin-104.

b. An unstable element undergoes two different decay reactions: beta decay to produce a material with a mass of 222 amu and alpha decay to astatine.

19. Bombarding $^{249}$Cf with $^{12}$C produced a transuranium element with a mass of 257 amu, plus several neutral subatomic particles. Identify the element and write a nuclear reaction for this transmutation.

20. One transuranium element, $^{253}$Es, is prepared by bombarding $^{238}$U with 15 neutrons. What is the other product of this reaction? Write a balanced transmutation reaction for this conversion.

21. Complete this radioactive decay series:

$$^{223}_{88}\text{Ra} \xrightarrow{\alpha} \text{Rn} \xrightarrow{\alpha} \text{Po} \xrightarrow{\alpha} \text{Pb} \xrightarrow{\beta^-} \text{Bi} \xrightarrow{\alpha} \text{Tl} \xrightarrow{\beta^-} \text{Pb}$$

22. Complete each nuclear fission reaction.

a. $^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{90}_{36}\text{Kr} + ? + 2{}^{1}_{0}\text{n}$
b. $? + {}^{1}_{0}\text{n} \rightarrow {}^{140}\text{Cs} + {}^{96}\text{Y} + 4{}^{1}_{0}\text{n}$

23. Complete each nuclear fission reaction.

a. $^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{145}_{57}\text{La} + ? + 3{}^{1}_{0}\text{n}$
b. $? + {}^{1}_{0}\text{n} \rightarrow {}^{95}_{42}\text{Mo} + {}^{139}_{57}\text{La} + 2{}^{1}_{0}\text{n} + 7{}^{0}_{-1}\beta$

24. A stable nuclide absorbs a neutron, emits an electron, and then splits into two α particles. Identify the nuclide.

25. Using $^{18}$O, how would you synthesize an element with atomic number 106 from $^{249}$Cf? Write a balanced nuclear equation for the reaction.

26. Using $^{10}$B and $^{252}$Cf, how would you synthesize an element with atomic number 103? Write a balanced nuclear equation for the reaction.

## Answers

3. a. α decay; $^{235}_{92}\text{U} \rightarrow {}^{4}_{2}\alpha + {}^{231}_{90}\text{Th}$
   b. α decay; $^{254}_{99}\text{Es} \rightarrow {}^{4}_{2}\alpha + {}^{250}_{97}\text{Bk}$
   c. β decay; $^{36}_{16}\text{S} \rightarrow {}^{0}_{-1}\beta + {}^{36}_{17}\text{Cl}$
   d. β decay; $^{99}_{42}\text{Mo} \rightarrow {}^{0}_{-1}\beta + {}^{99m}_{43}\text{Tc}$

5.

a. $^{208}_{84}\text{Po} \rightarrow {}^{4}_{2}\alpha + {}^{204}_{82}\text{Pb}$
b. $^{226}_{88}\text{Ra} \rightarrow {}^{4}_{2}\alpha + {}^{222}_{86}\text{Rn}$
c. $^{228}_{90}\text{Th} \rightarrow {}^{224}_{88}\text{Ra} + {}^{4}_{2}\alpha + \gamma$
d. $^{231}_{91}\text{Pa} \rightarrow {}^{227}_{89}\text{Ac} + {}^{4}_{2}\alpha + \gamma$
e. $^{166}_{67}\text{Ho} \rightarrow {}^{166}_{68}\text{Er} + {}^{0}_{-1}\beta + \gamma$
f. $^{226}_{89}\text{Ac} \rightarrow {}^{226}_{90}\text{Th} + {}^{0}_{-1}\beta + \gamma$

7.

a. $^{87}_{37}\text{Rb} \rightarrow {}^{87}_{38}\text{Sr} + {}^{0}_{-1}\beta$
b. $^{20}_{12}\text{Mg} \rightarrow {}^{20}_{11}\text{Na} + {}^{0}_{-1}\beta$
c. $^{268}_{109}\text{Mt} \rightarrow {}^{4}_{2}\alpha + {}^{264}_{107}\text{Bh}$

9.

a. α particle; $^{218}_{84}\text{Po} \rightarrow {}^{4}_{2}\alpha + {}^{214}_{82}\text{Pb}$
b. β particle; $^{32}_{14}\text{Si} \rightarrow {}^{0}_{-1}\beta + {}^{32}_{15}\text{P}$
c. γ ray; $^{57m}_{26}\text{Fe} \rightarrow {}^{57}_{26}\text{Fe} + \gamma$
d. β particle; $^{204}_{81}\text{Tl} \rightarrow {}^{0}_{-1}\beta + {}^{204}_{82}\text{Pb}$

11.

a. α emission; $^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\alpha + {}^{234}_{90}\text{Th}$
b. α emission; $^{208}_{84}\text{Po} \rightarrow {}^{204}_{82}\text{Pb} + {}^{4}_{2}\alpha$

c. β emission; ${}^{40}_{16}\mathrm{S} \rightarrow {}^{0}_{-1}\beta + {}^{40}_{17}\mathrm{Cl}$
d. γ emission; ${}^{93m}_{42}\mathrm{Mo} \rightarrow {}^{93}_{42}\mathrm{Mo} + \gamma$

13.

a. β decay; ${}^{216}_{84}\mathrm{Po} \rightarrow {}^{0}_{-1}\beta + {}^{216}_{85}\mathrm{At}$
b. α decay; ${}^{235}_{93}\mathrm{Np} \rightarrow {}^{4}_{2}\alpha + {}^{231}_{91}\mathrm{Pa}$
c. α decay; γ emission; ${}^{228}_{90}\mathrm{Th} \rightarrow {}^{224}_{88}\mathrm{Ra} + {}^{4}_{2}\alpha + \gamma$
d. β decay, γ emission; ${}^{231}_{91}\mathrm{Pa} \rightarrow {}^{231}_{92}\mathrm{U} + {}^{0}_{-1}\beta + \gamma$

17.

a. ${}^{80}_{35}\mathrm{Br} \rightarrow {}^{80}_{36}\mathrm{Kr} + {}^{0}_{-1}\beta$
b. ${}^{234}_{94}\mathrm{Pu} \rightarrow {}^{140}_{56}\mathrm{Ba} + {}^{92}_{38}\mathrm{Sr} + 2{}^{1}_{0}\mathrm{n}$

19. ${}^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{257}_{104}\mathrm{Rf} + 4{}^{1}_{0}\mathrm{n}$

23.

a. ${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{145}_{57}\mathrm{La} + {}^{88}_{35}\mathrm{Br} + 3{}^{1}_{0}\mathrm{n}$
b. ${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{95}_{42}\mathrm{Mo} + {}^{139}_{57}\mathrm{La} + 2{}^{1}_{0}\mathrm{n} + 7{}^{0}_{-1}\beta$

## 20.3: The Interaction of Nuclear Radiation with Matter

### Conceptual Problems

1. Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?
2. How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?
3. Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.
4. During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star “lit.” Explain the different reactions that dominate in the different stages of a star’s life cycle and their effect on the temperature of the star.
5. A line in a popular song from the 1960s by Joni Mitchell stated, “We are stardust….” Does this statement have any merit or is it just poetic? Justify your answer.
6. If the laws of physics were different and the primary element in the universe were boron-11 ($Z$ = 5), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

3. The raw material for all elements with $Z > 2$ is helium ($Z$ = 2), and fusion of helium nuclei will always produce nuclei with an even number of protons.

Answer

1.
4.
5.
6.

### Numerical Problems

1. Write a balanced nuclear reaction for the formation of each isotope.
    1. $^{27}$Al from two $^{12}$C nuclei
    2. $^{9}$Be from two $^{4}$He nuclei
2. At the end of a star’s life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.
    1. $^{106}$Pd from nickel-58

2. selenium-79 from iron-56

3. When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be “burned” in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

## 20.4: Thermodynamic Stability of the Atomic Nucleus

### Conceptual Problems

1. How do chemical reactions compare with nuclear reactions with respect to mass changes? Does either type of reaction violate the law of conservation of mass? Explain your answers.
2. Why is the amount of energy released by a nuclear reaction so much greater than the amount of energy released by a chemical reaction?
3. Explain why the mass of an atom is less than the sum of the masses of its component particles.
4. The stability of a nucleus can be described using two values. What are they, and how do they differ from each other?
5. In the days before true chemistry, ancient scholars (alchemists) attempted to find the philosopher’s stone, a material that would enable them to turn lead into gold. Is the conversion of Pb → Au energetically favorable? Explain why or why not.
6. Describe the energy barrier to nuclear fusion reactions and explain how it can be overcome.
7. Imagine that the universe is dying, the stars have burned out, and all the elements have undergone fusion or radioactive decay. What would be the most abundant element in this future universe? Why?
8. Numerous elements can undergo fission, but only a few can be used as fuels in a reactor. What aspect of nuclear fission allows a nuclear chain reaction to occur?
9. How are transmutation reactions and fusion reactions related? Describe the main impediment to fusion reactions and suggest one or two ways to surmount this difficulty.

### Numerical Problems

1. Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.
   a. $^{238}\text{Pa} \rightarrow \text{?} + \beta^-$
   b. $^{216}\text{Fr} \rightarrow \text{?} + \alpha$
   c. $^{199}\text{Bi} \rightarrow \text{?} + \beta^+$

2. Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.
   a. $^{194}\text{Tl} \rightarrow \text{?} + \beta^+$
   b. $^{171}\text{Pt} \rightarrow \text{?} + \alpha$
   c. $^{214}\text{Pb} \rightarrow \text{?} + \beta^-$

3. Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules per mole.
   a. $^{234}_{91}\text{Pa} \rightarrow \text{?} + {}^{0}_{-1}\beta$
   b. $^{226}_{88}\text{Ra} \rightarrow \text{?} + {}^{4}_{2}\alpha$

4. Using the information provided in Chapter 33, complete each reaction and then calculate the amount of energy released from each in kilojoules per mole.
   a. $^{60}_{27}\text{Co} \rightarrow \text{?} + {}^{0}_{-1}\beta$ (The mass of cobalt-60 is 59.933817 amu.)
   b. technicium-94 (mass = 93.909657 amu) undergoing fission to produce chromium-52 and potassium-40

5. Using the information provided in Chapter 33, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.
   a. the beta decay of bismuth-208 (mass = 207.979742 amu)

b. the formation of lead-206 by alpha decay

6. Using the information provided, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

   a. alpha decay of oxygen-16
   b. alpha decay to produce chromium-52

7. Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for $^{87}$Sr if the measured mass of $^{87}$Sr is 86.908877 amu.
8. Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for $^{60}$Ni.
9. The experimentally determined mass of $^{53}$Mn is 52.941290 amu. Find each of the following.

   a. the calculated mass
   b. the mass defect
   c. the nuclear binding energy
   d. the nuclear binding energy per nucleon

10. The experimentally determined mass of $^{29}$S is 28.996610 amu. Find each of the following.

    a. the calculated mass
    b. the mass defect
    c. the nuclear binding energy
    d. the nuclear binding energy per nucleon

11. Calculate the amount of energy that is released by the neutron-induced fission of $^{235}$U to give $^{141}$Ba, $^{92}$Kr (mass = 91.926156 amu), and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.
12. Calculate the amount of energy that is released by the neutron-induced fission of $^{235}$U to give $^{90}$Sr, $^{143}$Xe, and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.
13. Calculate the amount of energy released or required by the fusion of helium-4 to produce the unstable beryllium-8 (mass = 8.00530510 amu). Report your answer in kilojoules per mole. Do you expect this to be a spontaneous reaction?
14. Calculate the amount of energy released by the fusion of $^{6}$Li and deuterium to give two helium-4 nuclei. Express your answer in electronvolts per atom and kilojoules per mole.
15. How much energy is released by the fusion of two deuterium nuclei to give one tritium nucleus and one proton? How does this amount compare with the energy released by the fusion of a deuterium nucleus and a tritium nucleus, which is accompanied by ejection of a neutron? Express your answer in megaelectronvolts and kilojoules per mole. Pound for pound, which is a better choice for a fusion reactor fuel mixture?

## Answers

1.

   a. $^{238}_{91}\text{Pa} \rightarrow {}^{238}_{92}\text{U} + {}^{0}_{-1}\beta$; $-5.540 \times 10^{-16}$ kJ
   b. $^{216}_{87}\text{Fr} \rightarrow {}^{212}_{85}\text{At} + {}^{4}_{2}\alpha$; $-1.470 \times 10^{-15}$ kJ
   c. $^{199}_{83}\text{Bi} \rightarrow {}^{199}_{82}\text{Pb} + {}^{0}_{+1}\beta$; $-5.458 \times 10^{-16}$ kJ

3.

   a. $^{234}_{91}\text{Pa} \rightarrow {}^{234}_{92}\text{U} + {}^{0}_{-1}\beta$; $2.118 \times 10^{8}$ kJ/mol
   b. $^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha$; $4.700 \times 10^{8}$ kJ/mol

5.

   a. The beta decay of bismuth-208 to polonium is endothermic ($\Delta E$ = 1.400 MeV/atom, $1.352 \times 10^{8}$ kJ/mol).
   b. The formation of lead-206 by alpha decay of polonium-210 is exothermic ($\Delta E$ = −5.405 MeV/atom, $-5.218 \times 10^{8}$ kJ/mol).

7. 757 MeV/atom, 8.70 MeV/nucleon

9.

a. 53.438245 amu
b. 0.496955 amu
c. 463 MeV/atom
d. 8.74 MeV/nucleon

11. −173 MeV/atom; $1.67 \times 10^{10}$ kJ/mol

13. $\Delta E = +9.0 \times 10^{6}$ kJ/mol beryllium-8; no

15. D–D fusion: $\Delta E = -4.03$ MeV/tritium nucleus formed = $-3.89 \times 10^{8}$ kJ/mol tritium; D–T fusion: $\Delta E = -17.6$ MeV/tritium nucleus = $-1.70 \times 10^{9}$ kJ/mol; D–T fusion

## 20.5: Applied Nuclear Chemistry

### Conceptual Problems

1. In nuclear reactors, two different but interrelated factors must be controlled to prevent a mishap that could cause the release of unwanted radiation. How are these factors controlled?
2. What are the three principal components of a nuclear reactor? What is the function of each component?
3. What is meant by the term enrichment with regard to uranium for fission reactors? Why does the fuel in a conventional nuclear reactor have to be “enriched”?
4. The plot in a recent spy/action movie involved the threat of introducing stolen “weapons-grade” uranium, which consists of 93.3% $^{235}U$, into a fission reactor that normally uses a fuel containing about 3% $^{235}U$. Explain why this could be catastrophic.
5. Compare a heavy-water reactor with a light-water reactor. Why are heavy-water reactors less widely used? How do these two reactor designs compare with a breeder reactor?
6. Conventional light-water fission reactors require enriched fuel. An alternative reactor is the so-called heavy-water reactor. The components of the two different reactors are the same except that instead of using water ($H_2O$), the moderator in a heavy-water reactor is $D_2O$, known as “heavy water.” Because $D_2O$ is more efficient than $H_2O$ at slowing neutrons, heavy-water reactors do not require fuel enrichment to support fission. Why is $D_2O$ more effective at slowing neutrons, and why does this allow unenriched fuels to be used?
7. Isotopes emit γ rays in random directions. What difficulties do these emissions present for medical imaging? How are these difficulties overcome?
8. If you needed to measure the thickness of 1.0 mm plastic sheets, what type of radiation would you use? Would the radiation source be the same if you were measuring steel of a similar thickness? What is your rationale? Would you want an isotope with a long or short half-life for this device?

### Answers

1. Neutron flow is regulated by using control rods that absorb neutrons, whereas the speed of the neutrons produced by fission is controlled by using a moderator that slows the neutrons enough to allow them to react with nearby fissile nuclei.

7. It is difficult to pinpoint the exact location of the nucleus that decayed. In contrast, the collision of a positron with an electron causes both particles to be annihilated, and in the process, two gamma rays are emitted in opposite directions, which makes it possible to identify precisely where a positron emitter is located and to create detailed images of tissues.

### Numerical Problems

1. Palladium-103, which decays via electron capture and emits x-rays with an energy of $3.97 \times 10^{-2}$ MeV, is often used to treat prostate cancer. Small pellets of the radioactive metal are embedded in the prostate gland. This provides a localized source of radiation to a very small area, even though the tissue absorbs only about 1% of the x-rays. Due to its short half-life, all of the palladium will decay to a stable isotope in less than a year. If a doctor embeds 50 pellets containing 2.50 mg of $^{103}Pd$ in the prostate gland of a 73.9 kg patient, what is the patient’s radiation exposure over the course of a year?
2. Several medical treatments use cobalt-60m, which is formed by bombarding cobalt with neutrons to produce a highly radioactive gamma emitter that undergoes $4.23 \times 10^{16}$ emissions/(s·kg) of pure cobalt-60. The energy of the gamma emission is $5.86 \times 10^{-2}$ MeV. Write the balanced nuclear equation for the formation of this isotope. Is this a transmutation reaction? If a 55.3 kg patient received a 0.50 s exposure to a 0.30 kg cobalt-60 source, what would the exposure be in rads? Predict the potential side effects of this dose.

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