UC DAVIS: CHEM 2A GENERAL CHEMISTRY I



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UC Davis: Chem 2A General Chemistry I

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CHAPTER OVERVIEW

Unit 0: Primer

Chemistry is all around us "from the air we breathe to the food we eat" to the items at the super market that say “no chemicals added”. In fact, it is impossible to create something without using chemistry because chemistry consists of all matter. It allows us to answer questions as simple as why a candle goes out when a glass is placed over it to more complex questions such as does a candle actually burn in zero gravity? Chemistry is the study of matter and the changes it undergoes such as ice changing from the solid to liquid to gas phase. People have used it for things such as creating metal from an ore, dying fabric, and making cheese. Chemistry deals with different substances and how they can interact with each other to create a product.

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.

1.0: Chemistry in the Modern World
1.1: The Scientific Method
1.2: Properties of Matter
1.3: Classification of Matter
1.4: Measurement of Matter: SI (Metric Units)
1.5: Density and Percent Composition
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1.0: Chemistry in the Modern World

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.

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1.1: The Scientific Method

Skills to Develop

- 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 1.1.1).

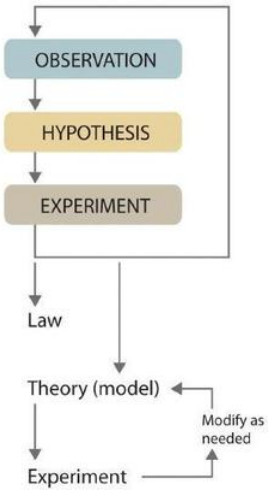


Figure 1.1.1: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

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 1.1.2 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 1.1.2 summarizes the application of the scientific method in this case.

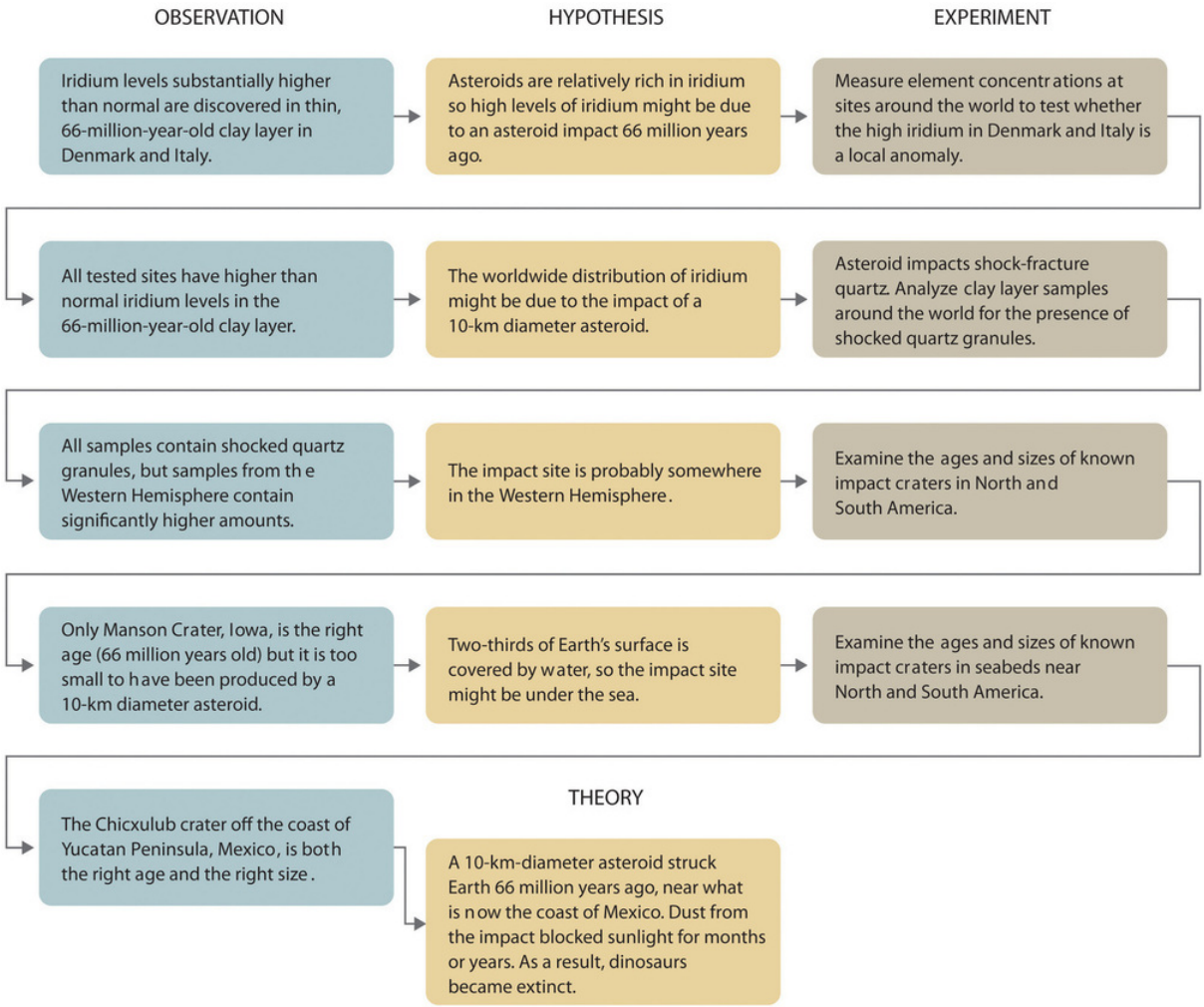


Figure 1.1.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

Example 1.1.1

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 1.1.1

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 1.1.1 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.

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1.2: Properties of Matter

Learning Objectives

- To separate physical from chemical properties and changes

All matter has physical and chemical properties. **Physical properties** are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). **Chemical properties** describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical properties can be extensive or intensive. **Extensive properties** vary with the amount of the substance and include mass, weight, and volume. **Intensive properties**, in contrast, do not depend on the amount of the substance; they include color, melting point, boiling point, electrical conductivity, and physical state at a given temperature. For example, elemental sulfur is a yellow crystalline solid that does not conduct electricity and has a melting point of 115.2°C, no matter what amount is examined (Figure 1.2.1). Scientists commonly measure intensive properties to determine a substance's identity, whereas extensive properties convey information about the amount of the substance in a sample.

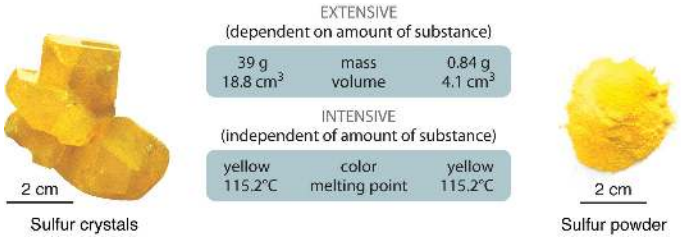


Figure 1.2.1: The Difference between Extensive and Intensive Properties of Matter. Because they differ in size, the two samples of sulfur have different extensive properties, such as mass and volume. In contrast, their intensive properties, including color, melting point, and electrical conductivity, are identical.

Although mass and volume are both extensive properties, their ratio is an important intensive property called **density** (ρ). Density is defined as mass per unit volume and is usually expressed in grams per cubic centimeter (g/cm^3). As mass increases in a given volume, density also increases. For example, lead, with its greater mass, has a far greater density than the same volume of air, just as a brick has a greater density than the same volume of Styrofoam. At a given temperature and pressure, the density of a pure substance is a constant:

$$density = \frac{mass}{volume} \rightarrow \rho = \frac{m}{v} \tag{1.2.1}$$

Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table 1.2.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table **1.2.1***: Densities of Common Substances*

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Physical Property and Change

Change in which the matter's physical appearance is altered, but composition remains unchanged, e.g., a change in state of matter. The three main states of matter are: Solid, Liquid, Gas

- Solid is distinguished by a fixed structure. Its shape and volume do not change. In a solid, atoms are tightly packed together in a fixed arrangement.
- Liquid is distinguished by its malleable shape (is able to form into the shape of its container), but constant volume. In a liquid, atoms are close together but not in a fixed arrangement.
- Gas is made up of atoms that are separate. However, unlike solid & liquid, a gas has no fixed shape and volume.



Different Definitions of Properties: https://youtu.be/n7UwjQJGh9Y

Example 1.2.1: Physical Change

When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass.



Figure 1.2.2: Ice Melting is a physical change

Chemical Properties and Change

- **Chemical Property is** Any characteristic that gives a sample of matter the ability/inability to undergo a change that alters its composition. Examples: Alkali metals react with water; Paper's ability to burn.
- **Chemical Change is a** Change in which one or more kinds of matter are transformed to new kinds of matter with altered compositions (or Chemical Reaction).

Example 1.2.2: Chemical Change

The combustion of magnetisum metal is a chemical change (Magnesium + Oxygen → Magnesium Oxide):

$$2Mg + O_2 \rightarrow 2MgO \tag{1.2.2}$$

The rusting of iron is a chemical change (Iron + Oxygen → Iron Oxide/ Rust):

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \quad (1.2.3)$$

Using the components of composition and properties, we have the ability to distinguish one sample of matter from the others.



Different Definitions of Changes: https://youtu.be/OiLaMHigCuo

References

1. Petrucci, Bissonnette, Herring, Madura. General Chemistry: Principles and Modern Applications. Tenth ed. Upper Saddle River, NJ 07458: Pearson Education Inc., 2011.
2. Cracolice, Peters. Basics of introductory Chemistry An active Learning Approach. Second ed. Belmont, CA 94001:Brooks/Cole, 2007.

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1.3: Classification of Matter

Learning Objectives

- To classify matter.

Chemists study the structures, physical properties, and chemical properties of material substances. These consist of **matter**, which is anything that occupies space and has mass. Gold and iridium are matter, as are peanuts, people, and postage stamps. Smoke, smog, and laughing gas are matter. Energy, light, and sound, however, are not matter; ideas and emotions are also not matter.

The **mass** of an object is the quantity of matter it contains. Do not confuse an object's mass with its **weight**, which is a force caused by the gravitational attraction that operates on the object. Mass is a fundamental property of an object that does not depend on its location.In physical terms, the mass of an object is directly proportional to the force required to change its speed or direction. A more detailed discussion of the differences between weight and mass and the units used to measure them is included in Essential Skills 1 (Section 1.9). Weight, on the other hand, depends on the location of an object. An astronaut whose mass is 95 kg weighs about 210 lb on Earth but only about 35 lb on the moon because the gravitational force he or she experiences on the moon is approximately one-sixth the force experienced on Earth. For practical purposes, weight and mass are often used interchangeably in laboratories. Because the force of gravity is considered to be the same everywhere on Earth's surface, 2.2 lb (a weight) equals 1.0 kg (a mass), regardless of the location of the laboratory on Earth.

Under normal conditions, there are three distinct states of matter: solids, liquids, and gases. **Solids** are relatively rigid and have fixed shapes and volumes. A rock, for example, is a solid. In contrast, **liquids** have fixed volumes but flow to assume the shape of their containers, such as a beverage in a can. **Gases**, such as air in an automobile tire, have neither fixed shapes nor fixed volumes and expand to completely fill their containers. Whereas the volume of gases strongly depends on their temperature and **pressure** (the amount of force exerted on a given area), the volumes of liquids and solids are virtually independent of temperature and pressure. Matter can often change from one physical state to another in a process called a **physical change**. For example, liquid water can be heated to form a gas called steam, or steam can be cooled to form liquid water. However, such changes of state do not affect the chemical composition of the substance.

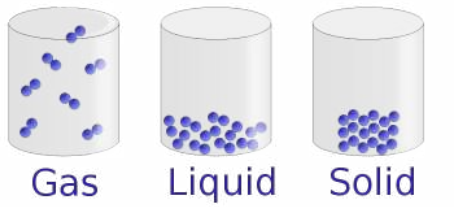


Figure 1.3.1: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia

Pure Substances and Mixtures

A pure chemical substance is any matter that has a fixed chemical composition and characteristic properties. Oxygen, for example, is a pure chemical substance that is a colorless, odorless gas at 25°C. Very few samples of matter consist of pure substances; instead, most are mixtures, which are combinations of two or more pure substances in variable proportions in which the individual substances retain their identity. Air, tap water, milk, blue cheese, bread, and dirt are all mixtures. If all portions of a material are in the same state, have no visible boundaries, and are uniform throughout, then the material is **homogeneous**. Examples of homogeneous mixtures are the air we breathe and the tap water we drink. Homogeneous mixtures are also called solutions. Thus air is a solution of nitrogen, oxygen, water vapor, carbon dioxide, and several other gases; tap water is a solution of small amounts of several substances in water. The specific compositions of both of these solutions are not fixed, however, but depend on both source and location; for example, the composition of tap water in Boise, Idaho, is not the same as the composition of tap water in Buffalo, New York. Although most solutions we encounter are liquid, solutions can also be solid. The gray substance still used by some dentists to fill tooth cavities is a complex solid solution that contains 50% mercury and 50% of a powder that contains mostly silver, tin, and copper, with small amounts of zinc and mercury. Solid solutions of two or more metals are commonly called alloys.

If the composition of a material is not completely uniform, then it is **heterogeneous** (e.g., chocolate chip cookie dough, blue cheese, and dirt). Mixtures that appear to be homogeneous are often found to be heterogeneous after microscopic examination. Milk, for example, appears to be homogeneous, but when examined under a microscope, it clearly consists of tiny globules of fat and protein dispersed in water. The components of heterogeneous mixtures can usually be separated by simple means. Solid-liquid mixtures such as sand in water or tea leaves in tea are readily separated by filtration, which consists of passing the mixture through a barrier, such as a strainer, with holes or pores that are smaller than the solid particles. In principle, mixtures of two or more solids, such as sugar and salt, can be separated by microscopic inspection and sorting. More complex operations are usually necessary, though, such as when separating gold nuggets from river gravel by panning. First solid material is filtered from river water; then the solids are separated by inspection. If gold is embedded in rock, it may have to be isolated using chemical methods.



Figure 1.3.2: A Heterogeneous Mixture. Under a microscope, whole milk is actually a heterogeneous mixture composed of globules of fat and protein dispersed in water. Figure used with permission from Wikipedia

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. **Distillation** makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

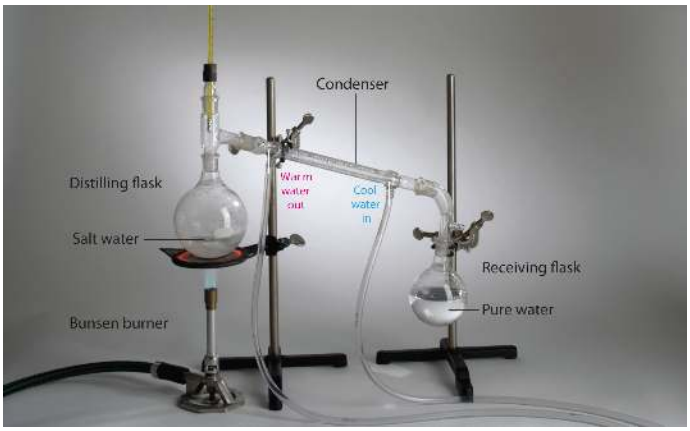


Figure 1.3.3: The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States.

Crystallization separates mixtures based on differences in solubility, a measure of how much solid substance remains dissolved in a given amount of a specified liquid. Most substances are more soluble at higher temperatures, so a mixture of two or more substances can be dissolved at an elevated temperature and then allowed to cool slowly. Alternatively, the liquid, called the solvent,

may be allowed to evaporate. In either case, the least soluble of the dissolved substances, the one that is least likely to remain in solution, usually forms crystals first, and these crystals can be removed from the remaining solution by filtration.



Figure 1.3.4: The Crystallization of Sodium Acetate from a Concentrated Solution of Sodium Acetate in Water. The addition of a small “seed” crystal (a) causes the compound to form white crystals, which grow and eventually occupy most of the flask. Video can be found here: https://www.youtube.com/watch?v=BLq5NibwV5g

Most mixtures can be separated into pure substances, which may be either elements or compounds. An **element**, such as gray, metallic sodium, is a substance that cannot be broken down into simpler ones by chemical changes; a **compound**, such as white, crystalline sodium chloride, contains two or more elements and has chemical and physical properties that are usually different from those of the elements of which it is composed. With only a few exceptions, a particular compound has the same elemental composition (the same elements in the same proportions) regardless of its source or history. The chemical composition of a substance is altered in a process called a **chemical change**. The conversion of two or more elements, such as sodium and chlorine, to a chemical compound, sodium chloride, is an example of a chemical change, often called a chemical reaction. Currently, about 115 elements are known, but millions of chemical compounds have been prepared from these 115 elements. The known elements are listed in the periodic table.

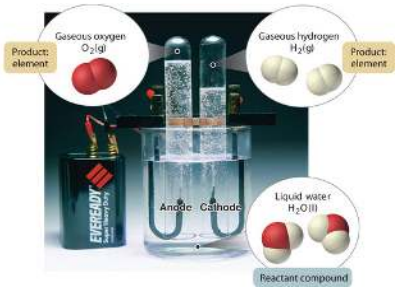


Figure 1.3.5: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

In general, a reverse chemical process breaks down compounds into their elements. For example, water (a compound) can be decomposed into hydrogen and oxygen (both elements) by a process calledelectrolysis. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (Figure 1.3.5). A similar technique is used on a vast scale to obtain pure aluminum, an element, from its ores, which are mixtures of compounds. Because a great deal of energy is required for electrolysis, the cost of electricity is by far the greatest expense incurred in manufacturing pure aluminum. Thus recycling aluminum is both cost-effective and ecologically sound. The overall organization of matter and the methods used to separate mixtures are summarized in Figure 1.3.6.

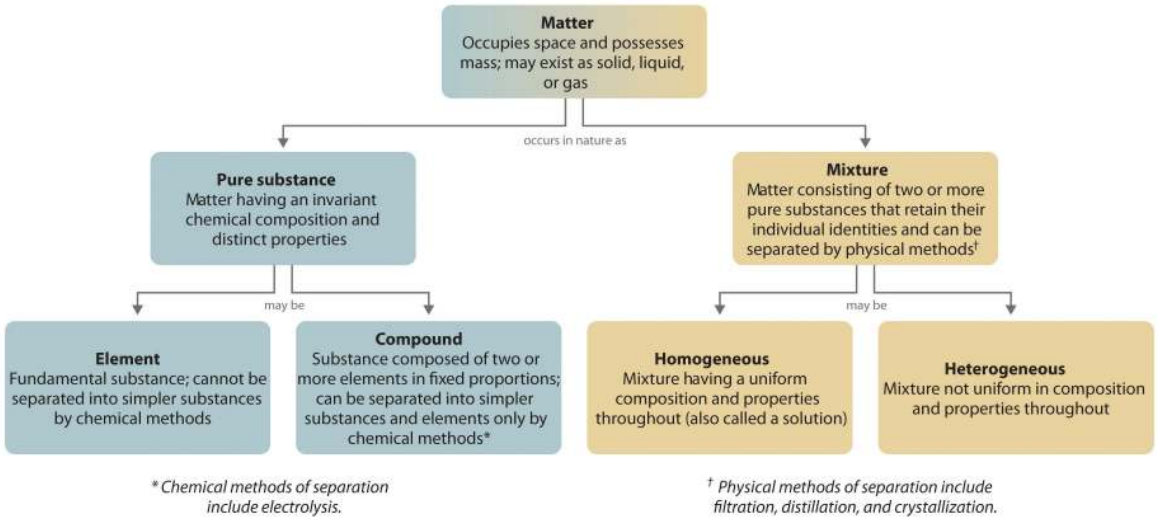


Figure 1.3.6: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 1.3.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea
b. freshly squeezed orange juice
c. a compact disc
d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution

a. **A** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration. **B** Because the composition of the solution is uniform throughout, it is a homogeneous mixture.
b. **A** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure. B Because its composition is not uniform throughout, orange juice is a heterogeneous mixture.
c. **A** A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure. **B** The regions of different composition indicate that a compact disc is a heterogeneous mixture.
d. **A** Aluminum oxide is a single, chemically pure compound.
e. **A** Selenium is one of the known elements.

Exercise 1.3.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. white wine
b. mercury
c. ranch-style salad dressing

d. table sugar (sucrose)

Answer

a. solution
b. element
c. heterogeneous mixture
d. compound



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

Summary

Matter can be classified according to physical and chemical properties. Matter is anything that occupies space and has mass. The three states of matter are solid, liquid, and gas. A physical change involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of mixtures of pure substances, which can be homogeneous (uniform in composition) or heterogeneous (different regions possess different compositions and properties). Pure substances can be either chemical compounds or elements. Compounds can be broken down into elements by chemical reactions, but elements cannot be separated into simpler substances by chemical means. The properties of substances can be classified as either physical or chemical. Scientists can observe physical properties without changing the composition of the substance, whereas chemical properties describe the tendency of a substance to undergo chemical changes (chemical reactions) that change its chemical composition. Physical properties can be intensive or extensive. Intensive properties are the same for all samples; do not depend on sample size; and include, for example, color, physical state, and melting and boiling points. Extensive properties depend on the amount of material and include mass and volume. The ratio of two extensive properties, mass and volume, is an important intensive property called density.

Contributors and Attributions

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1.4: Measurement of Matter: SI (Metric Units)

Learning Objectives

- To identify the basic units of measurement of the seven fundamental properties
- Describe the names and abbreviations of the *SI base units* and the *SI decimal prefixes*.
- Define the *liter* and the *metric ton* in these units.
- Explain the meaning and use of *unit dimensions*; state the dimensions of *volume*.
- State the quantities that are needed to define a *temperature scale*, and show how these apply to the *Celsius*, *Kelvin*, and *Fahrenheit* temperature scales.
- Explain how a Torricellian *barometer* works.

Have you ever estimated a distance by "stepping it off"— that is, by counting the number of steps required to take you a certain distance? Or perhaps you have used the width of your hand, or the distance from your elbow to a fingertip to compare two dimensions. If so, you have engaged in what is probably the first kind of measurement ever undertaken by primitive mankind. The results of a measurement are always expressed on some kind of a *scale* that is defined in terms of a particular kind of *unit*. The first scales of distance were likely related to the human body, either directly (the length of a limb) or indirectly (the distance a man could walk in a day).

Ångstrom	1E−6 cm
Astronomical unit	1.495E8 km
Bolt (U.S., cloth)	120 ft
Cable length	720 ft
Chain (engineer's)	100 ft
Chain (surveyor's)	0.1 furlong
Cubit	18 in
Ell	45 in
Foot (U.S.)	12 in
Foot (British)	0.4 pace
Furlong	1/8 mile
Hand	4 in
Inch (U.S.)	1/12 ft
Inch (British)	1/36 yard
League	3 miles
Light year	9.46E12 km
Mile (U.S., staute)	5280 ft
Mile (nautical)	1.853 km
Nail (British)	2.25 in
Pace (British)	30 in
Parsec	3.084E13 km
Point (printer's)	1/72 in
Rope (British)	20 ft
Span	9 in

Figure 1.4.1: Current and past units of distance

As civilization developed, a wide variety of measuring scales came into existence, many for the same quantity (such as length), but adapted to particular activities or trades. Eventually, it became apparent that in order for trade and commerce to be possible, these scales had to be defined in terms of standards that would allow measures to be verified, and, when expressed in different units (bushels and pecks, for example), to be correlated or converted.

History of Units

Over the centuries, hundreds of measurement units and scales have developed in the many civilizations that achieved some literate means of recording them. Some, such as those used by the Aztecs, fell out of use and were largely forgotten as these civilizations died out. Other units, such as the various systems of measurement that developed in England, achieved prominence through extension of the Empire and widespread trade; many of these were confined to specific trades or industries. The examples shown here are only some of those that have been used to measure length or distance. The history of measuring units provides a fascinating reflection on the history of industrial development.

The most influential event in the history of measurement was undoubtedly the French Revolution and the Age of Rationality that followed. This led directly to the metric system that attempted to do away with the confusing multiplicity of measurement scales by reducing them to a few fundamental ones that could be combined in order to express any kind of quantity. The metric system spread rapidly over much of the world, and eventually even to England and the rest of the U.K. when that country established closer economic ties with Europe in the latter part of the 20th Century. The United States is presently the only major country in which "metrication" has made little progress within its own society, probably because of its relative geographical isolation and its vibrant internal economy.

Science, being a truly international endeavor, adopted metric measurement very early on; engineering and related technologies have been slower to make this change, but are gradually doing so. Even the within the metric system, however, a variety of units were employed to measure the same fundamental quantity; for example, energy could be expressed within the metric system in units of ergs, electron-volts, joules, and two kinds of calories. This led, in the mid-1960s, to the adoption of a more basic set of units, the *Systeme Internationale* (*SI*) units that are now recognized as the standard for science and, increasingly, for technology of all kinds.

The Seven *SI* Base Units and Decimal Prefixes

In principle, any physical quantity can be expressed in terms of only seven base units (Table 1.4.1), with each base unit defined by a standard described in the NIST Web site.

Table 1.4.1: The Seven Base Units

Property	Unit	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
temperature (absolute)	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

A few special points about some of these units are worth noting:

- The base unit of **mass** is unique in that a decimal prefix (Table 1.4.2) is built into it; i.e., the base SI unit is not the *gram*.
- The base unit of **time** is the only one that is not metric. Numerous attempts to make it so have never garnered any success; we are still stuck with the 24:60:60 system that we inherited from ancient times. The ancient Egyptians of around 1500 BC invented the 12-hour day, and the 60:60 part is a remnant of the base-60 system that the Sumerians used for their astronomical calculations around 100 BC.
- Of special interest to Chemistry is the *mole*, the base unit for expressing the **quantity of matter**. Although the number is not explicitly mentioned in the official definition, chemists define the mole as Avogadro's number (approximately 6.02×10^{23}) of anything.

Owing to the wide range of values that quantities can have, it has long been the practice to employ prefixes such as milli and mega to indicate decimal fractions and multiples of metric units. As part of the SI standard, this system has been extended and formalized (Table 1.4.2).

Table 1.4.2: Prefixes used to scale up or down base units

Prefix	Abbreviation	Multiplier		Prefix	Abbreviation	Multiplier
peta	P	10^{18}		deci	s	10^{-1}
tera	T	10^{12}		centi	c	10^{-2}
giga	G	10^{9}		milli	m	10^{-3}
mega	M	10^{6}		micro	μ	10^{-6}
kilo	k	10^{3}		nano	n	10^{-9}
hecto	h	10^{2}		pico	p	10^{-12}
deca	da	10		femto	f	10^{-15}

Pseudo-Si Units

There is a category of units that are "honorary" members of the SI in the sense that it is acceptable to use them along with the base units defined above. These include such mundane units as the hour, minute, and degree (of angle), etc., but the three shown here are of particular interest to chemistry, and you will need to know them.

liter (litre)	L	1 L = 1 dm^3 = 10^{-3} m^3
metric ton	t	1 t = 10^3 kg
united atomic mass unit (amu)	u	1 u = 1.66054×10^{-27} kg

Derived Units and Dimensions

Most of the physical quantities we actually deal with in science and also in our daily lives, have units of their own: volume, pressure, energy and electrical resistance are only a few of hundreds of possible examples. It is important to understand, however, that all of these can be expressed in terms of the SI base units; they are consequently known as *derived units*. In fact, most physical quantities can be expressed in terms of one or more of the following five fundamental units:

- mass (M)
- length (L)
- time (T)
- electric charge (Q)
- temperature (Θ theta)

Consider, for example, the unit of *volume*, which we denote as V. To measure the volume of a rectangular box, we need to multiply the lengths as measured along the three coordinates:

$$V = x \cdot y \cdot z \tag{1.4.1}$$

We say, therefore, that volume has the dimensions of length-cubed:

$$dim\{V\} = L^3 \tag{1.4.2}$$

Thus the units of volume will be m^3 (in the SI) or cm^3, ft^3 (English), etc. Moreover, any formula that calculates a volume must contain within it the L^3 dimension; thus the volume of a sphere is $4/3\pi r^3$. The *dimensions* of a unit are the powers which M, L, t, Q and Q must be given in order to express the unit. Thus,

$$dim\{V\} = M^0 L^3 T^0 Q^0 \Theta^0 \tag{1.4.3}$$

as given above.

There are several reasons why it is worthwhile to consider the dimensions of a unit.

1. Perhaps the most important use of dimensions is to help us understand the relations between various units of measure and thereby get a better understanding of their physical meaning. For example, a look at the dimensions of the frequently confused electrical terms resistance and resistivity should enable you to explain, in plain words, the difference between them.
2. By the same token, the dimensions essentially tell you how to calculate any of these quantities, using whatever specific units you wish. (Note here the distinction between dimensions and units.)
3. Just as you cannot add apples to oranges, an expression such as $a = b + cx^2$ is meaningless unless the dimensions of each side are identical. (Of course, the two sides should work out to the same units as well.)
4. Many quantities must be dimensionless— for example, the variable x in expressions such as $\log x$, e^x, and $\sin x$. Checking through the dimensions of such a quantity can help avoid errors.

The formal, detailed study of dimensions is known as *dimensional analysis* and is a topic in any basic physics course.

Example 1.4.1

Find the dimensions of energy.

Solution

When mechanical work is performed on a body, its energy increases by the amount of work done, so the two quantities are equivalent and we can concentrate on work. The latter is the product of the force applied to the object and the distance it is displaced. From Newton's law, force is the product of mass and acceleration, and the latter is the rate of change of velocity, typically expressed in meters per second per second. Combining these quantities and their dimensions yields the result shown in Table 1.4.1.

Table 1.4.3: Dimensions of units commonly used in Chemistry

Q	M	L	t	quantity	SI unit, other typical units
1				electric charge	coulomb
	1			mass	kilogram, gram, metric ton, pound
		1		length	meter, foot, mile
			1	time	second, day, year
		3		volume	liter, cm^3, quart, fluidounce
	1	–3		density	kg m^{-3}, g cm^{-3}
	1	1	–2	force	newton, dyne
	1	–1	–2	pressure	pascal, atmosphere, torr
	1	2	–2	energy	joule, erg, calorie, electron-volt
	1	2	–3	power	watt
1	1	2	–2	electric potential	volt
1			–1	electric current	ampere
1	1	1	–2	electric field intensity	volt m^{-1}
–2	1	2	–1	electric resistance	ohm
2	1	3	–1	electric resistivity	
2	–1	–2	1	electric conductance	siemens, mho

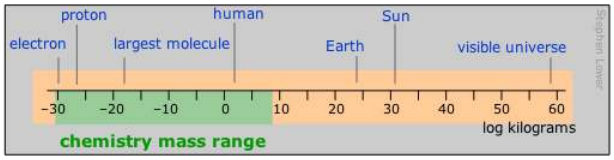
Dimensional analysis is widely employed when it is necessary to convert one kind of unit into another, and chemistry students often use it in "chemical arithmetic" calculations, in which context it is also known as the "Factor-Label" method. In this section, we will look at some of the quantities that are widely encountered in Chemistry, and at the units in which they are commonly expressed. In doing so, we will also consider the actual range of values these quantities can assume, both in nature in general, and also within the subset of nature that chemistry normally addresses. In looking over the various units of measure, it is interesting to note that their unit values are set close to those encountered in everyday human experience

Mass is not weight

These two quantities are widely confused. Although they are often used synonymously in informal speech and writing, they have different dimensions: *weight* is the *force* exerted on a mass by the local gravational field:

$$f = ma = mg \tag{1.4.4}$$

where g is the acceleration of gravity. While the nominal value of the latter quantity is 9.80 m s^{-2} at the Earth's surface, its exact value varies locally. Because it is a force, the SI unit of weight is properly the *newton*, but it is common practice (except in physics classes!) to use the terms "weight" and "mass" interchangeably, so the units *kilograms* and *grams* are acceptable in almost all ordinary laboratory contexts.

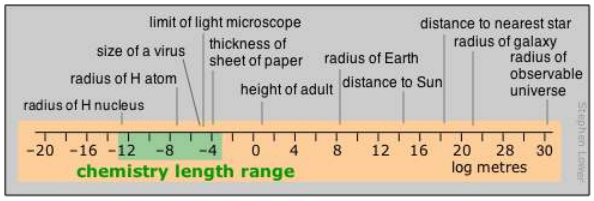


Please note that in this diagram and in those that follow, the numeric scale represents the *logarithm* of the number shown. For example, the mass of the electron is 10^{-30} kg.

The range of masses spans 90 orders of magnitude, more than any other unit. The range that chemistry ordinarily deals with has greatly expanded since the days when a microgram was an almost inconceivably small amount of material to handle in the laboratory; this lower limit has now fallen to the atomic level with the development of tools for directly manipulating these particles. The upper level reflects the largest masses that are handled in industrial operations, but in the recently developed fields of geochemistry and enivonmental chemistry, the range can be extended indefinitely. Flows of elements between the various regions of the environment (atmosphere to oceans, for example) are often quoted in teragrams.

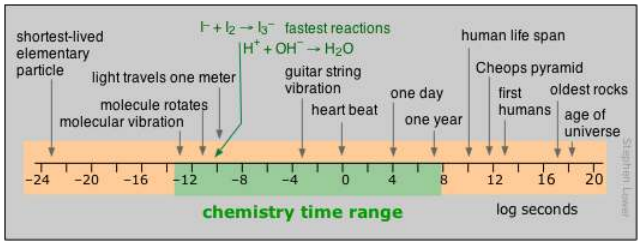
Length

Chemists tend to work mostly in the moderately-small part of the distance range. Those who live in the lilliputian world of crystal- and molecular structures and atomic radii find the *picometer* a convenient currency, but one still sees the older non-SI unit called the *Ångstrom* used in this context; 1Å = 10^{-10} m = 100pm. Nanotechnology, the rage of the present era, also resides in this realm. The largest polymeric molecules and colloids define the top end of the particulate range; beyond that, in the normal world of doing things in the lab, the *centimeter* and occasionally the *millimeter* commonly rule.



Time

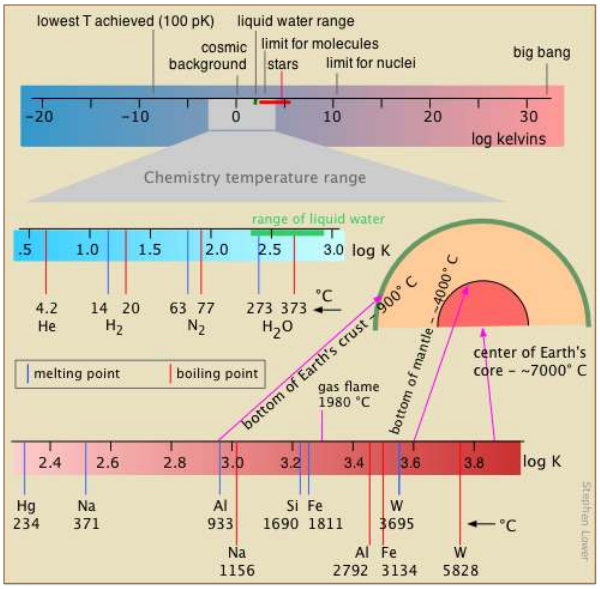
For humans, time moves by the heartbeat; beyond that, it is the motions of our planet that count out the hours, days, and years that eventually define our lifetimes. Beyond the few thousands of years of history behind us, those years-to-the-powers-of-tens that are the fare for such fields as evolutionary biology, geology, and cosmology, cease to convey any real meaning for us. Perhaps this is why so many people are not very inclined to accept their validity.



Most of what actually takes place in the chemist's test tube operates on a far shorter time scale, although there is no limit to how slow a reaction can be; the upper limits of those we can directly study in the lab are in part determined by how long a graduate student can wait around before moving on to gainful employment. Looking at the microscopic world of atoms and molecules themselves, the time scale again shifts us into an unreal world where numbers tend to lose their meaning. You can gain some appreciation of the duration of a nanosecond by noting that this is about how long it takes a beam of light to travel between your two outstretched hands. In a sense, the material foundations of chemistry itself are defined by time: neither a new element nor a molecule can be recognized as such unless it lasts long enough to have its "picture" taken through measurement of its distinguishing properties.

Temperature

Temperature, the measure of thermal intensity, spans the narrowest range of any of the base units of the chemist's measurement toolbox. The reason for this is tied into temperature's meaning as a measure of the intensity of thermal kinetic energy. Chemical change occurs when atoms are jostled into new arrangements, and the weakness of these motions brings most chemistry to a halt as absolute zero is approached. At the upper end of the scale, thermal motions become sufficiently vigorous to shake molecules into atoms, and eventually, as in stars, strip off the electrons, leaving an essentially reaction-less gaseous fluid, or plasma, of bare nuclei (ions) and electrons.



The degree is really an *increment* of temperature, a fixed fraction of the distance between two defined reference points on a *temperature scale*.

Although rough means of estimating and comparing temperatures have been around since AD 170, the first mercury thermometer and temperature scale were introduced in Holland in 1714 by Gabriel Daniel Fahrenheit. Fahrenheit established three fixed points on his thermometer. Zero degrees was the temperature of an ice, water, and salt mixture, which was about the coldest temperature that could be reproduced in a laboratory of the time. When he omitted salt from the slurry, he reached his second fixed point when the water-ice combination stabilized at "the thirty-second degree." His third fixed point was "found at the ninety-sixth degree, and the spirit expands to this degree when the thermometer is held in the mouth or under the armpit of a living man in good health."

After Fahrenheit died in 1736, his thermometer was recalibrated using 212 degrees, the temperature at which water boils, as the upper fixed point. Normal human body temperature registered 98.6 rather than 96. In 1743, the Swedish astronomer Anders Celsius devised the aptly-named *centigrade* scale that places exactly 100 degrees between the two reference points defined by the freezing and boiling points of water.

When we say that the temperature is so many degrees, we must specify the particular scale on which we are expressing that temperature. A temperature scale has two defining characteristics, both of which can be chosen arbitrarily:

- The temperature that corresponds to 0° on the scale;
- The magnitude of the *unit increment* of temperature– that is, the size of the *degree*.

To express a temperature given on one scale in terms of another, it is necessary to take both of these factors into account. The key to temperature conversions is easy if you bear in mind that between the so-called ice- and steam-points of water there are 180 Fahrenheit degrees, but only 100 Celsius degrees, making the F° 100/180 = 5/9 the magnitude of the C°. Note the distinction between "°C" (a *temperature*) and "C°" (a temperature *increment*). Because the ice point is at 32°F, the two scales are offset by this amount. If you remember this, there is no need to memorize a conversion formula; you can work it out whenever you need it.

Near the end of the 19th Century when the physical significance of temperature began to be understood, the need was felt for a temperature scale whose zero really means zero— that is, the complete absence of thermal motion. This gave rise to the *absolute temperature scale* whose zero point is –273.15 °C, but which retains the same degree magnitude as the Celsius scale. This eventually got renamed after Lord Kelvin (William Thompson); thus the Celsius degree became the *kelvin*. Thus we can now express an increment such as five C° as "five kelvins"

The "other" Absolute Scale

In 1859 the Scottish engineer and physicist William J. M. Rankine proposed an absolute temperature scale based on the Fahrenheit degree. Absolute zero (0° Ra) corresponds to –459.67°F. The Rankine scale has been used extensively by those same American and English engineers who delight in expressing heat capacities in units of BTUs per pound per F°.

The importance of absolute temperature scales is that absolute temperatures can be entered directly in all the fundamental formulas of physics and chemistry in which temperature is a variable.

Pressure

Pressure is the measure of the *force* exerted on a unit area of surface. Its SI units are therefore newtons per square meter, but we make such frequent use of pressure that a derived SI unit, the *pascal*, is commonly used:

$$1\ Pa = 1\ N\ m^{-2} \tag{1.4.5}$$

The concept of pressure first developed in connection with studies relating to the atmosphere and vacuum that were carried out in the 17th century.

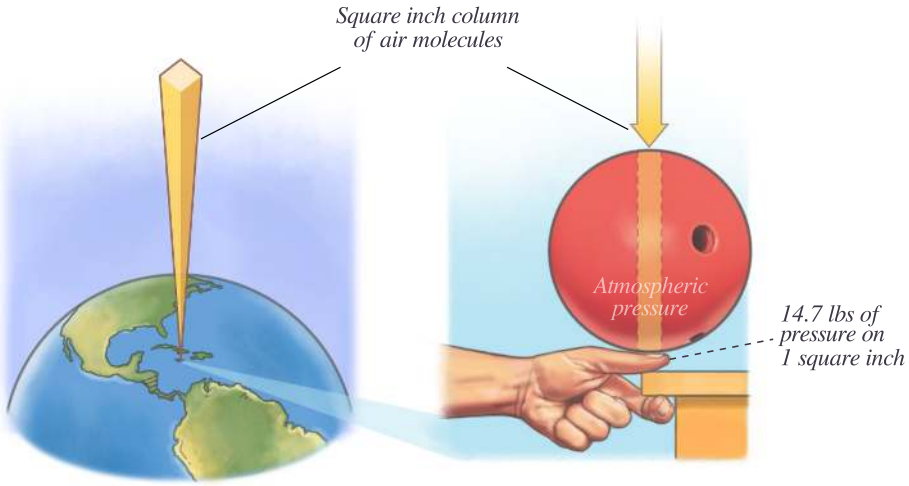


Figure 1.4.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail. (CC BY-NC; Ümit Kaya)

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car below. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved

under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.



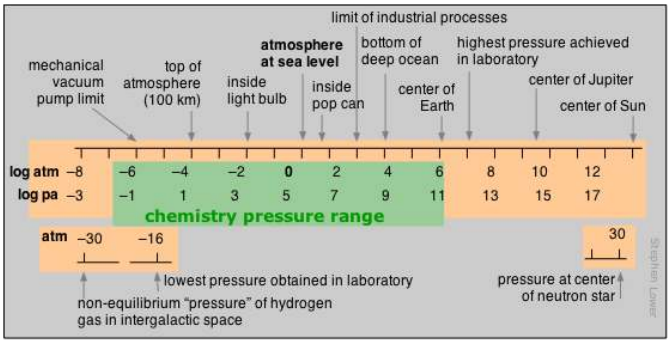
Video 1.4.1: A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased. A smaller scale demonstration of this phenomenon is briefly explained.

The molecules of a gas are in a state of constant thermal motion, moving in straight lines until experiencing a collision that exchanges momentum between pairs of molecules and sends them bouncing off in other directions. This leads to a completely random distribution of the molecular velocities both in speed and direction— or it would in the absence of the Earth's gravitational field which exerts a tiny downward force on each molecule, giving motions in that direction a very slight advantage. In an ordinary container this effect is too small to be noticeable, but in a very tall column of air the effect adds up: the molecules in each vertical layer experience more downward-directed hits from those above it. The resulting force is quickly randomized, resulting in an increased pressure in that layer which is then propagated downward into the layers below.

At sea level, the total mass of the sea of air pressing down on each 1-cm^2 of surface is about 1034 g, or 10340 kg m^{-2}. The force (weight) that the Earth's gravitional acceleration g exerts on this mass is

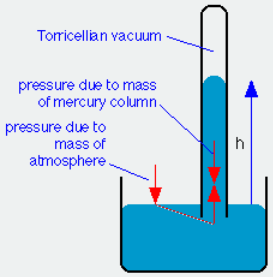
$$f = ma = mg = (10340\ kg)(9.81\ m\ s^{-2}) = 1.013 \times 10^5\ kg\ m\ s^{-2} = 1.013 \times 10^5\ N \tag{1.4.6}$$

resulting in a pressure of 1.013 × 10^5 n m^{-2} = 1.013 × 10^5 Pa. The actual pressure at sea level varies with atmospheric conditions, so it is customary to define standard atmospheric pressure as 1 atm = 1.01325 x 10^5 Pa or 101.325 kPa. Although the standard atmosphere is not an SI unit, it is still widely employed. In meteorology, the *bar*, exactly 1.000 × 10^5 = 0.967 atm, is often used.



The Barometer

In the early 17th century, the Italian physicist and mathematician Evangalisto Torricelli invented a device to measure atmospheric pressure. The Torricellian *barometer* consists of a vertical glass tube closed at the top and open at the bottom. It is filled with a liquid, traditionally mercury, and is then inverted, with its open end immersed in the container of the same liquid. The liquid level in the tube will fall under its own weight until the downward force is balanced by the vertical force transmitted hydrostatically to the column by the downward force of the atmosphere acting on the liquid surface in the open container. Torricelli was also the first to recognize that the space above the mercury constituted a vacuum, and is credited with being the first to create a vacuum.



One *standard atmosphere* will support a column of mercury that is 760 mm high, so the “millimeter of mercury”, now more commonly known as the *torr*, has long been a common pressure unit in the sciences: 1 atm = 760 torr.

Summary

The natural sciences begin with ***observation,*** and this usually involves ***numerical measurements*** of quantities such as length, volume, density, and temperature. Most of these quantities have ***units*** of some kind associated with them, and these units must be retained when you use them in calculations. Measuring units can be defined in terms of a very small number of fundamental ones that, through "dimensional analysis", provide insight into their derivation and meaning, and must be understood when converting between different unit systems.

Contributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.5: Density and Percent Composition

Learning Objectives

- To be introduced to the concepts of Density and Percent Composition as important properties of matter.

Density and percent composition are important properties in chemistry. Each have basic components as well as broad applications. Components of density are: mass and volume, both of which can be more confusing than at first glance. An application of the concept of density is determining the volume of an irregular shape using a known mass and density. Determining Percent Composition requires knowing the mass of entire object or molecule and the mass of its components.

Introduction

Which one weighs more, a kilogram of feathers or a kilogram of bricks? Though many people will say that a kilogram of bricks is heavier, they actually weigh the same! However, many people are caught up by the concept of density ρ, which causes them to answer the question incorrectly. A kilogram of feathers clearly takes up more space, but this is because it is less "dense." But what is density, and how can we determine it?

In the laboratory, density can be used to identify an element, while percent composition is used to determine the amount, by mass, of each element present in a chemical compound. In daily life, density explains everything from why boats float to why air bubbles will try to escape from soda. It even affects your health because bone density is very important. Similarly, percent composition is commonly used to make animal feed and compounds such as the baking soda found in your kitchen.

Density

Density is a physical property found by dividing the mass of an object by its volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 grams per cubic centimeter. This means that whether you have one gram or one kilogram of the sample, the density will never vary. The equation, as we already know, is as follows:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \tag{1.5.1}$$

or just

$$\rho = \frac{m}{v} \tag{1.5.2}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relation of mass and volume. But let us break it down one step further. What are mass and volume? We cannot understand density until we know its parts: mass and volume. The following two sections will teach you all the information you need to know about volume and mass to properly solve and manipulate the density equation.

Mass

Mass concerns the quantity of matter in an object. The SI unit for mass is the kilogram (kg), although grams (g) are commonly used in the laboratory to measure smaller quantities. Often, people mistake weight for mass. Weight concerns the force exerted on an object as a function of mass and gravity. This can be written as

$$\text{Weight} = \text{mass} \times \text{gravity} \tag{1.5.3}$$

$$Weight = mg$$

Since on the earth, the g in the equation is equal to one, weight and mass are considered equal on earth. It is important to note that although g is equal to one in basic equations, it actually differs throughout earth by a small fraction depending on location; gravity at the equator is less than at the poles. On other astronomical objects, gravity and hence weight, highly differs. This is because weight changes due to variations in gravity and acceleration. The mass, however, of a 1 kg cube will continue to be 1 kg whether it is on the top of a mountain, the bottom of the sea, or on the moon.

Another important difference between mass and weight is how they are measured. Weight is measured with a scale, while mass must be measured with a balance. Just as people confuse mass and weight, they also confuse scales and balances. A balance

counteracts the effects of gravity while a scale incorporates it. There are two types of balances found in the laboratory: electronic and manual. With a manual balance, you find the unknown mass of an object by adjusting or comparing known masses until equilibrium is reached. With an electronic balance, which is what you will work with in the UC Davis laboratory, the mass is found by electronic counterbalancing with little effort from the user. An electronic balance can be far more accurate than any other balance and is easier to use, but they are expensive. Also, keep in mind that all instruments used in the laboratory have systematic errors.

Volume

Volume describes the quantity of three dimensional space than an object occupies. The SI unit for volume is meters cubed (m^3), but milliliters (mL), centimeters cubed (cm^3), and liters (L) are more common in the laboratory. There are many equations to find volume. Here are just a few of the easy ones:

$$\text{Volume} = (\text{length})^3$$

or

$$\text{Volume} = (\text{length})(\text{width})(\text{height})$$

or

$$\text{Volume} = (\text{base area})(\text{height})$$

Density: A Further Investigation

Units

We know all of density's components, so let's take a closer look at density itself. The unit most widely used to express density is g/cm^3 or g/mL, though the SI unit for density is technically kg/m^3. Grams per centimeter cubed is equivalent to grams per milliliter (g/cm^3 = g/mL). To solve for density, simply follow the equation 1.5.1. For example, if you had a metal cube with mass 7.0 g and volume 5.0 cm^3, the density would be $\rho = \frac{7\ g}{5\ cm^3} = 1.4\ g/cm^3$. Sometimes, you have to convert units to get the correct units for density, such as mg to g or in^3 to cm^3.

Density in the Periodic Table

Density can be used to help identify an unknown element. Of course, you have to know the density of an element with respect to other elements. Below is a table listing the density of a few elements from the Periodic Table at standard conditions for temperature and pressure, or STP. STP corresponds to a temperature of 273 K (0° Celsius) and 1 atmosphere of pressure.

Table 1.5.1: Density of Elements at standard temperature and pressure

Element Name and Symbol	Density (g/cm3)	Atomic Number
Hydrogen (H)	0.09	1
Helium (He)	0.18	2
Aluminum (Al)	2.7	13
Zinc (Zn)	7.13	30
Tin (Sn)	7.31	50
Iron (Fe)	7.87	26
Nickel (Ni)	8.9	28
Cobalt (Co)	8.9	27
Copper (Cu)	8.96	29
Silver (Ag)	10.5	47
Lead (Pb)	11.35	82
Mercury (Hg)	11.55	80

Element Name and Symbol	Density (g/cm3)	Atomic Number
Gold (Au)	19.32	79
Platinum (Pt)	21.45	78
Osmium (Os)	22.6	76

As can be seen from the table, the most dense element is Osmium (Os) with a density of 22.6 g/cm^3. The least dense element is Hydrogen (H) with a density of 0.09 g/cm^3.

Density and Temperature

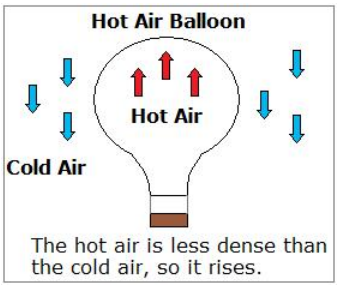
Density generally decreases with increasing temperature and likewise increases with decreasing temperatures. This is because volume differs according to temperature. Volume increases with increasing temperature. Below is a table showing the density of pure water with differing temperatures.

Table 1.5.2: Density fo water as a function of Temperature

Temperature (C)	Density (g/cm3)
100	0.9584
80	0.9718
60	0.9832
40	0.9922
30	0.9957
25	0.997
22	0.9978
20	0.9982
15	0.9991
10	0.9997
4	1.000
0 (liquid)	0.9998
0 (solid)	0.9150

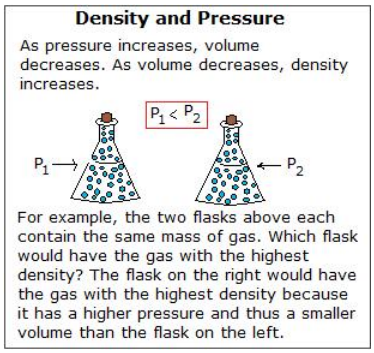
As can be seen from Table 1.5.2, the density of water decreases with increasing temperature. Liquid water also shows an exception to this rule from 0 degrees Celsius to 4 degrees Celsius, where it increases in density instead of decreasing as expected. Looking at the table, you can also see that ice is less dense than water. This is unusual as solids are generally denser than their liquid counterparts. Ice is less dense than water due to hydrogen bonding. In the water molecule, the hydrogen bonds are strong and compact. As the water freezes into the hexagonal crystals of ice, these hydrogen bonds are forced farther apart and the volume increases. With this volume increase comes a decrease in density. This explains why ice floats to the top of a cup of water: the ice is less dense.

Even though the rule of density and temperature has its exceptions, it is still useful. For example, it explains how hot air balloons work.



Density and Pressure

Density increases with increasing pressure because volume decreases as pressure increases. And since density=mass/volume , the lower the volume, the higher the density. This is why all density values in the Periodic Table are recorded at STP, as mentioned in the section "Density and the Periodic Table." The decrease in volume as related to pressure is explained in Boyle's Law: $P_1V_1 = P_2V_2$ where P = pressure and V = volume. This idea is explained in the figure below.



Archimedes' Principle

The Greek scientist Archimedes made a significant discovery in 212 B.C. The story goes that Archimedes was asked to find out for the King if his goldsmith was cheating him by replacing his gold for the crown with silver, a cheaper metal. Archimedes did not know how to find the volume of an irregularly shaped object such as the crown, even though he knew he could distinguish between elements by their density. While meditating on this puzzle in a bath, Archimedes recognized that when he entered the bath, the water rose. He then realized that he could use a similar process to determine the density of the crown! He then supposedly ran through the streets naked shouting "Eureka," which means "I found it!" in Latin.

Archimedes then tested the king's crown by taking a genuine gold crown of equal mass and comparing the densities of the two. The king's crown displaced more water than the gold crown of the same mass, meaning that the king's crown had a greater volume and thus had a smaller density than the real gold crown. The king's "gold" crown, therefore, was not made of pure gold. Of course, this tale is disputed today because Archimedes was not precise in all his measurements, which would make it hard to determine accurately the differences between the two crowns.

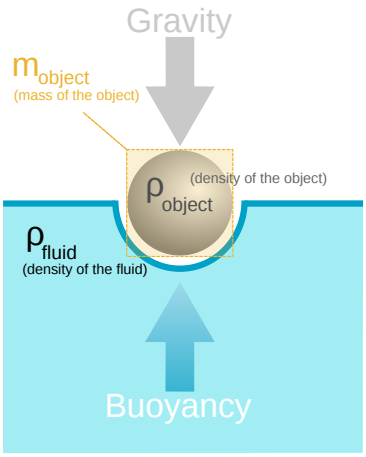


Figure 1.5.2: The forces at work in buoyancy. Note that the object is floating because the upward force of buoyancy is equal to the downward force of gravity. (CC BY-SA 3.0; Yupi666 via Wikipedia.

Archimedes' Principle states that if an object has a greater density than the liquid that it is placed into, it will sink and displace a volume of liquid equal to its own. If it has a smaller density, it will float and displace a mass of liquid equal to its own. If the density is equal, it will not sink or float (Figure 1.5.2). The principle explains why balloons filled with helium float. Balloons, as we learned in the section concerning density and temperature, float because they are less dense than the surrounding air. Helium is less dense than the atmospheric air, so it rises. Archimedes' Principle can also be used to explain why boats float. Boats, including all the air space, within their hulls, are far less dense than water. Boats made of steel can float because they displace their mass in water without submerging all the way. The table below gives the densities of a few liquids to put things into perspective.

Table 1.5.3: Density of Common Liquids

Liquid	Density in kg/m^3	Density in g/cm^3
2-Methoxyethanol	964.60	0.9646
Acetic Acid	1049.10	1.049
Acetone	789.86	0.7898
Alcohol, ethyl	785.06	0.7851
Alcohol, methyl	786.51	0.7865
Ammonia	823.35	0.8234
Benzene	873.81	0.8738
Water, pure	1000.00	1.000

Percent Composition

Percent composition is very simple. **Percent composition** tells you by mass what percent of each element is present in a compound. A chemical compound is the combination of two or more elements. If you are studying a chemical compound, you may want to find the percent composition of a certain element within that chemical compound. The equation for percent composition is

$$\text{Percent Composition} = \frac{\text{Total mass of element present}}{\text{Molecular mass}} \times 100\% \tag{1.5.4}$$

If you want to know the percent composition of the elements in an compound, follow these steps:

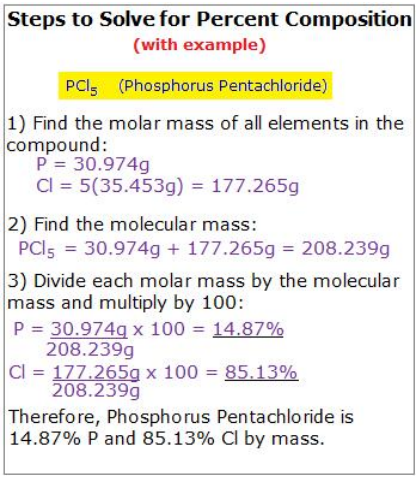
Steps to Solve:

1. Find the molar mass of all the elements in the compound in grams per mole.
2. Find the molecular mass of the entire compound.
3. Divide the component's molar mass by the entire molecular mass.
4. You will now have a number between 0 and 1. Multiply it by 100 to get percent composition!

Tips for solving:

1. The compounds will always add up to 100%, so in a binary compound, you can find the % of the first element, then do 100%-(% first element) to get (% second element)
2. If using a calculator, you can store the overall molar mass to a variable such as "A". This will speed up calculations, and reduce typographical errors.

These steps are outlined in the figure below.



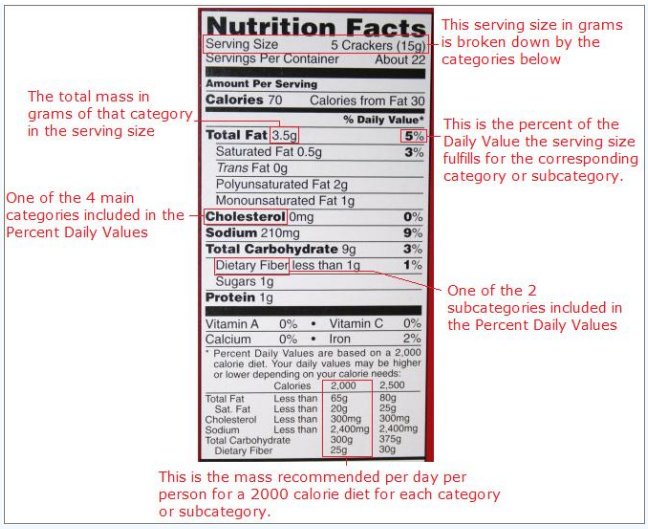
For another example, if you wanted to know the percent composition of hydrochloric acid (HCl), first find the molar mass of Hydrogen. H = 1.00794g. Now find the molecular mass of HCl: 1.00794g + 35.4527g = 36.46064g. Follow steps 3 and 4: (1.00794g/36.46064g) x 100 = 2.76% Now just subtract to find the percent by mass of Chlorine in the compound: 100%-2.76% = 97.24% Therefore, HCl is 2.76% Hydrogen and 97.24% Chlorine by mass.

Percent Composition in Everyday Life

Percent composition plays an important role in everyday life. It is more than just the amount of chlorine in your swimming pool because it concerns everything from the money in your pocket to your health and how you live. The next two sections describe percent composition as it relates to you.

Example 1.5.1: Nutritional Labels

The nutrition label found on the container of every bit of processed food sold by the local grocery store employs the idea of percent composition. On all nutrition labels, a known serving size is broken down in five categories: Total Fat, Cholesterol, Sodium, Total Carbohydrate, and Protein. These categories are broken down into further subcategories, including Saturated Fat and Dietary Fiber. The mass for each category, except Protein, is then converted to percent of Daily Value. Only two subcategories, Saturated Fat and Dietary Fiber are converted to percent of Daily Value. The Daily Value is based on a the mass of each category recommended per day per person for a 2000 calorie diet. The mass of protein is not converted to percent because their is no recommended daily value for protein. Following is a picture outlining these ideas.



For example, if you wanted to know the percent by mass of the daily value for sodium you are eating when you eat one serving of the food with this nutrition label, then go to the category marked sodium. Look across the same row and read the percent written. If you eat one serving of this food, then you will have consumed about 9% of your daily recommended value for sodium. To find the percent mass of fat in the whole food, you could divide 3.5 grams by 15 grams, and see that this snack is 23.33% fat.

Example 1.5.2: The Lucky Penny

The penny should be called "the lucky copper *coated* coin." The penny has not been made of solid copper since part of 1857. After 1857, the US government started adding other cheaper metals to the mix. The penny, being only one cent, is literally not worth its weight in copper. People could melt copper pennies and sell the copper for more than the pennies were worth. After 1857, nickel was mixed with the more expensive copper. After 1864, the penny was made of bronze. Bronze is 95% copper and 5% zinc and tin. For one year, 1943, the penny had no copper in it due to the expense of the World War II. It was just zinc coated steel. After 1943 until 1982, the penny went through periods where it was brass or bronze.



Figure 1.5.3: Today, the penny in America is 2.5% copper with 97.5% zinc. The copper coats the outside of the penny while the inner portion is zinc. For comparison's sake, the penny in Canada is 94% steel, 1.5% nickel, and 4.5% copper.

The percent composition of a penny may actually affect health, particularly the health of small children and pets. Since the newer pennies are made mainly of zinc instead of copper, they are a danger to a child's health if ingested. Zinc is very susceptible to acid. If the thin copper coating is scratched and the hydrochloric acid present in the stomach comes into contact with the zinc core it could cause ulcers, anemia, kidney and liver damage, or even death in severe cases. Three important factors in penny ingestion are time, pH of the stomach, and amount of pennies ingested. Of course, the more pennies swallowed, the more danger of an overdose of zinc. The more acidic the environment, the more zinc will be released in less time. This zinc is then absorbed and sent to the liver where it begins to cause damage. In this kind of situation, time is of the essence. The faster the penny is removed, the less zinc is absorbed. If the penny or pennies are not removed, organ failure and death can occur.

Below is a picture of a scratched penny before and after it had been submerged in lemon juice. Lemon juice has a similar pH of 1.5-2.5 when compared to the normal human stomach after food has been consumed. Time elapsed: 36 hours.



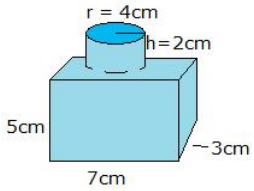

As you can see, the copper is vastly unharmed by the lemon juice. That's why pennies made before 1982 with mainly copper (except the 1943 penny) are relatively safe to swallow. Chances are they would pass through the digestive system naturally before any damage could be done. Yet, it is clear that the zinc was partially dissolved even though it was in the lemon juice for only a limited amount of time. Therefore, the percent composition of post 1982 pennies is hazardous to your health and the health of your pets if ingested.

Problems

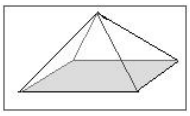
Following are examples of different types of percent composition and density problems.

Density Problems: These problems are meant to be easy in the beginning and then gradually become more challenging. Unless otherwise stated, answers should be in **g/mL** or the equivalent **g/cm^3**.

1. If you have a 2.130 mL sample of acetic acid with mass 0.002234 kg, what is the density?
2. Calculate the density of a .03020 L sample of ethyl alcohol with a mass of 23.71002 g.
3. Find the density of a sample that has a volume of 36.5 L and a mass of 10.0 kg.
4. Find the volume in mL of an object that has a density of 10.2 g/L and a mass of 30.0 kg.
5. Calculate the mass in grams of an object with a volume of 23.5 mL and density of 10.0 g/L.
6. Calculate the density of a rectangular prism made of metal. The dimensions of the prism are: 5 cm by 4 cm by 5 cm. The metal has a mass of 50 grams.
7. Find the density of an unknown liquid in a beaker. The beaker's mass is 165 g when there is no liquid present. With the unknown liquid, the total mass is 309 g. The volume of the unknown is 125 mL.
8. Determine the density in g/L of an unknown with the following information. A 55 gallon tub weighs 137.5lb when empty and 500.0 lb when filled with the unknown.
9. A ring has a mass of 5.00g and a volume of 0.476 mL. Is it pure silver?
10. What is the density of the solid in the image if the mass is 40 g? Make your answer have 3 significant figures.



11. Below is a model of a pyramid found at an archeological dig made of an unknown substance. It is too large to find the volume by submerging it in water. Also, the scientists refuse to remove a piece to test because this pyramid is a part of history. Its height is 150.0m. The length of its base is 75.0m and the width is 50.0m. The mass of this pyramid is 5.50x10^{5}kg. What is the density?



Percent Composition Problems: These problems will follow the same pattern of difficulty as those of density.

12. Calculate the percent by mass of each element in Cesium Fluoride (CsF).
13. Calculate the percent by mass of each element present in carbon tetrachloride (CCl_4)
14. A solution of salt and water is 33.0% salt by mass and has a density of 1.50 g/mL. What mass of the salt in grams is in 5.00L of this solution?

15. A solution of water and HCl contains 25% HCl by mass. The density of the solution is 1.05 g/mL. If you need 1.7g of HCl for a reaction, what volume of this solution will you use?
16. A solution containing 42% NaOH by mass has a density of 1.30 g/mL. What mass, in kilograms, of NaOH is in 6.00 L of this solution?

Answers

Here are the solutions to the listed practice problems.

Density Problem Solutions

1. 1.049 g/mL
2. 0.7851 g/mL
3. 0.274 g/mL
4. 2.94 x 10^6 mL
5. 0.3.27 kg
6. 0.5 g/cm^3
7. 1.15 g/mL
8. 790 g/L
9. Yes
10. 0.195 g/cm^3
11. 29.3 g/cm^3

Percent Composition Problem Solutions

12. CsF is 87.5% Cs and 12.5% F by mass
13. CCl_4 is 92.2% Cl and 7.8% C by mass
14. 2480 g
15. 6.5 mL
16. 3.26 kg

References

1. AUTOR , ARQUIMEDES , and Thomas Little . The Works of Archimedes . Courier Dover Publications, 2002.
2. Chande, D. and T. Fisher (2003). "Have a Penny? Need a Penny? Eliminating the One-Cent Coin from Circulation." Canadian Public Policy/Analyse de Politiques **29**(4): 511-517.
3. Jefferson, T. (1999). "A Thought for Your Pennies." JAMA **281**(2): 122.
4. Petrucci , Ralph , William Harwood , and Geoffrey Herring . Principles and Modern Application. ninth . New Jersey : Peason Eduation , 2007.
5. Rauch, F., H. Plotkin, et al. (2003). "Bone Mass, Size, and Density in Children and Adolescents with Osteogenesis Imperfecta: Effect of Intravenous Pamidronate Therapy." Journal of Bone and Mineral Research **18**: 610-614.
6. Richardson, J., S. Gwaltney-Brant, et al. (2002). "Zinc Toxicosis from Penny Ingestion in Dogs." Vet Med **97**(2): 96-99.
7. Tate, J. "Archimedes' Discoveries: A Closer Look."

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1.6: Uncertainties in Scientific Measurements

Learning Objectives

- To introduce the fundamental mathematical skills you will need to complete basic chemistry questions and problems

All measurements have a degree of uncertainty regardless of precision and accuracy. This is caused by two factors, the limitation of the measuring instrument (systematic error) and the skill of the experimenter making the measurements (random error).

Introduction

The graduated buret in Figure 1.6.1 contains a certain amount of water (with yellow dye) to be measured. The amount of water is somewhere between 19 ml and 20 ml according to the marked lines. By checking to see where the bottom of the meniscus lies, referencing the ten smaller lines, the amount of water lies between 19.8 ml and 20 ml. The next step is to estimate the uncertainty between 19.8 ml and 20 ml. Making an approximate guess, the level is less than 20 ml, but greater than 19.8 ml. We then report that the measured amount is approximately 19.9 ml. The graduated cylinder itself may be distorted such that the graduation marks contain inaccuracies providing readings slightly different from the actual volume of liquid present.



Figure 1.6.1: A meniscus as seen in a burette of colored water. '20.00 mL' is the correct depth measurement.

Systematic vs. Random Error

Systematic errors: When we use tools meant for measurement, we assume that they are correct and accurate, however measuring tools are not always right. In fact, they have errors that naturally occur called **systematic errors**. Systematic errors tend to be consistent in magnitude and/or direction. If the magnitude and direction of the error is known, accuracy can be improved by additive or proportional corrections. **Additive correction** involves adding or subtracting a constant adjustment factor to each measurement; **proportional correction** involves multiplying the measurement(s) by a constant.

Random errors: Sometimes called human error, random error is determined by the experimenter's skill or ability to perform the experiment and read scientific measurements. These errors are random since the results yielded may be too high or low. Often random error determines the precision of the experiment or limits the precision. For example, if we were to time a revolution of a steadily rotating turnable, the random error would be the reaction time. Our reaction time would vary due to a delay in starting (an underestimate of the actual result) or a delay in stopping (an overestimate of the actual result). Unlike systematic errors, random errors vary in magnitude and direction. It is possible to calculate the average of a set of measured positions, however, and that average is likely to be more accurate than most of the measurements.

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. Figure 1.6.1 help to understand the difference between precision (small expected difference between multiple measurements) and accuracy (difference between the result and a known value).

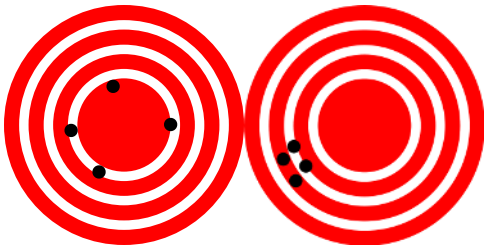


Figure 1.6.1: (left) Random error are characterized by high accuracy and low Precision (right) Systematic errors are characterized by high precision but low accuracy. (Public Domain; DarkEvil)

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:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.6.1}$$

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

$$deviation = |\text{measurement} - \text{average}| \tag{1.6.2}$$

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:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.6.3}$$

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

$$\frac{1.125\ g + 1.158\ g + 1.067\ g}{3} = 1.117\ g \tag{1.6.4}$$

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

$$\frac{0.008\ g + 0.041\ g + 0.050\ g}{3} = 0.033\ g \tag{1.6.5}$$

The precision of this set of measurements is therefore

$$\frac{0.033\ g}{1.117\ g} \times 100 = 3.0\% \tag{1.6.6}$$

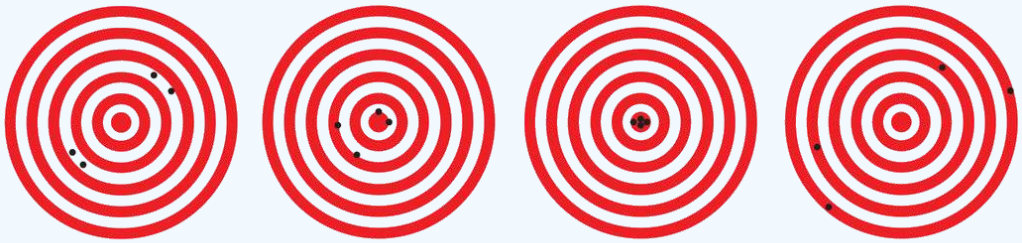
When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique.

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.

Example 1.6.1

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

Example 1.6.2

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

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

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.

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

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

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:

$$1 ft = 12 in$$

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 8.00×10^{-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.

Example 1.6.3

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

Example 1.6.4

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 + 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.



Significant Figures: https://youtu.be/E-OAkZglfO8

Problems

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

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1.7: Significant Figures

Learning Objectives

- Give an example of a measurement whose number of significant digits is clearly too great, and explain why.
- State the purpose of rounding off, and describe the information that must be known to do it properly.
- Round off a number to a specified number of significant digits.
- Explain how to round off a number whose second-most-significant digit is 9.
- Carry out a simple calculation that involves two or more observed quantities, and express the result in the appropriate number of significant figures.

The numerical values we deal with in science (and in many other aspects of life) represent measurements whose values are never known exactly. Our pocket-calculators or computers don't know this; they treat the numbers we punch into them as "pure" mathematical entities, with the result that the operations of arithmetic frequently yield answers that are physically ridiculous even though mathematically correct. The purpose of this unit is to help you understand why this happens, and to show you what to do about it.

Digits: Significant and otherwise

Consider the two statements shown below:

- **"The population of our city is 157,872."**
- **"The number of registered voters as of Jan 1 was 27,833.**

Which of these would you be justified in dismissing immediately? Certainly not the second one, because it probably comes from a database which contains one record for each voter, so the number is found simply by counting the number of records. The first statement cannot possibly be correct. Even if a city's population could be defined in a precise way (Permanent residents? Warm bodies?), how can we account for the minute-by minute changes that occur as people are born and die, or move in and move away?

What is the difference between the two population numbers stated above? The first one expresses a quantity that cannot be known exactly — that is, it carries with it a degree of uncertainty. It is quite possible that the last census yielded precisely 157,872 records, and that this might be the "population of the city" for legal purposes, but it is surely not the "true" population. To better reflect this fact, one might list the population (in an atlas, for example) as **157,900** or even **158,000**. These two quantities have been rounded off to four and three significant figures, respectively, and the have the following meanings:

- **157900** (the significant digits are underlined here) implies that the population is believed to be within the range of about 157850 to about 157950. In other words, the population is 157900±50. The "plus-or-minus 50" appended to this number means that we consider the absolute uncertainty of the population measurement to be 50 – (–50) = 100. We can also say that the relative uncertainty is 100/157900, which we can also express as 1 part in 1579, or 1/1579 = 0.000633, or about 0.06 percent.
- The value **158000** implies that the population is likely between about 157500 and 158500, or 158000±500. The absolute uncertainty of 1000 translates into a relative uncertainty of 1000/158000 or 1 part in 158, or about 0.6 percent.

Which of these two values we would report as "the population" will depend on the degree of confidence we have in the original census figure; if the census was completed last week, we might round to four significant digits, but if it was a year or so ago, rounding to three places might be a more prudent choice. In a case such as this, there is no really objective way of choosing between the two alternatives.

This illustrates an important point: the concept of *significant digits* has less to do with mathematics than with our confidence in a measurement. This confidence can often be expressed numerically (for example, the height of a liquid in a measuring tube can be read to ±0.05 cm), but when it cannot, as in our population example, we must depend on our personal experience and judgment.

So, what is a significant digit? According to the usual definition, it is all the numerals in a measured quantity (counting from the left) whose values are considered as known exactly, plus one more whose value could be one more or one less:

- In "157900" (four significant digits), the left most three digits are known exactly, but the fourth digit, "9" could well be "8" if the "true value" is within the implied range of 157850 to 157950.
- In "*158*000" (three significant digits), the left most two digits are known exactly, while the third digit could be either "7" or "8" if the true value is within the implied range of 157500 to 158500.



Although rounding off always leads to the loss of numeric information, what we are getting rid of can be considered to be “numeric noise” that does not contribute to the quality of the measurement. The purpose in rounding off is to avoid expressing a value to a greater degree of precision than is consistent with the uncertainty in the measurement.

Implied Uncertainty

If you know that a balance is accurate to within 0.1 mg, say, then the uncertainty in any measurement of mass carried out on this balance will be ±0.1 mg. Suppose, however, that you are simply told that an object has a length of 0.42 cm, with no indication of its precision. In this case, all you have to go on is the number of digits contained in the data. Thus the quantity “0.42 cm” is specified to 0.01 unit in 0 42, or one part in 42 . The implied relative uncertainty in this figure is 1/42, or about 2%. The precision of any numeric answer calculated from this value is therefore limited to about the same amount.

Rounding Error

It is important to understand that the number of significant digits in a value provides only a rough indication of its precision, and that information is lost when rounding off occurs. Suppose, for example, that we measure the weight of an object as 3.28 g on a balance believed to be accurate to within ±0.05 gram. The resulting value of 3.28±.05 gram tells us that the true weight of the object could be anywhere between 3.23 g and 3.33 g. The absolute uncertainty here is 0.1 g (±0.05 g), and the relative uncertainty is 1 part in 32.8, or about 3 percent.

How many significant digits should there be in the reported measurement? Since only the left most “3” in “3.28” is certain, you would probably elect to round the value to 3.3 g. So far, so good. But what is someone else supposed to make of this figure when they see it in your report? The value “3.3 g” suggests an *implied uncertainty* of 3.3±0.05 g, meaning that the true value is likely between 3.25 g and 3.35 g. This range is 0.02 g below that associated with the original measurement, and so rounding off has introduced a bias of this amount into the result. Since this is less than half of the ±0.05 g uncertainty in the weighing, it is not a very serious matter in itself. However, if several values that were rounded in this way are combined in a calculation, the rounding-off errors could become significant.

Rules for Rounding

The standard rules for rounding off are well known. Before we set them out, let us agree on what to call the various components of a numeric value.

- The *most significant digit* is the left most digit (not counting any leading zeros which function only as placeholders and are never significant digits.)
- If you are rounding off to ***n*** significant digits, then the *least significant digit* is the ***n***th digit from the most significant digit. The least significant digit can be a zero.
- The first non-significant digit is the ***n***+1th digit.

Rounding-off rules

- If the first non-significant digit is less than 5, then the least significant digit remains unchanged.
- If the first non-significant digit is greater than 5, the least significant digit is incremented by 1.
- If the first non-significant digit is 5, the least significant digit can either be incremented or left unchanged (*see below!*)
- All non-significant digits are removed.

Fantasies about fives

Students are sometimes told to increment the least significant digit by 1 if it is odd, and to leave it unchanged if it is even. One wonders if this reflects some idea that even numbers are somehow “better” than odd ones! (The ancient superstition is just the opposite, that only the odd numbers are "lucky".)

In fact, you could do it equally the other way around, incrementing only the even numbers. If you are only rounding a single number, it doesn't really matter what you do. However, when you are rounding a series of numbers that will be used in a calculation, if you treated each first nonsignificant 5 in the same way, you would be over- or understating the value of the rounded number, thus accumulating round-off error. Since there are equal numbers of even and odd digits, incrementing only the one kind will keep this kind of error from building up. You could do just as well, of course, by flipping a coin!

Table 1.7.1: Examples of rounding-off

number to round	number of significant digits	result	comment
34.216	3	34.2	First non-significant digit (1) is less than 5, so number is simply truncated.
2.252	2	2.2 or 2.3	First non-significant digit is 5, so least sig. digit can either remain unchanged or be incremented.
39.99	3	40.0	Crossing "decimal boundary", so all numbers change.
85,381	3	85,400	The two zeros are just placeholders
0.04597	3	0.0460	The two leading zeros are not significant digits.

Rounding up the Nines

Suppose that an object is found to have a weight of 3.98 ± 0.05 g. This would place its true weight somewhere in the range of **3.93** g to **4.03** g. In judging how to round this number, you count the number of digits in “3.98” that are known exactly, and you find none! Since the “4” is the left most digit whose value is uncertain, this would imply that the result should be rounded to one significant figure and reported simply as 4 g. An alternative would be to bend the rule and round off to two significant digits, yielding 4.0 g. How can you decide what to do? In a case such as this, you should look at the implied uncertainties in the two values, and compare them with the uncertainty associated with the original measurement.

Table 1.7.2

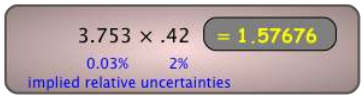
rounded value	implied max	implied min	absolute uncertainty	relative uncertainty
3.98 g	3.985 g	3.975 g	±.005 g or 0.01 g	1 in 400, or 0.25%
4 g	4.5 g	3.5 g	±.5 g or 1 g	1 in 4, 25%
4.0 g	**4.05 g**	**3.95 g**	**±.05 g or 0.1 g**	**1 in 40, 2.5%**

Clearly, rounding off to two digits is the only reasonable course in this example. Observed values should be rounded off to the number of digits that most accurately conveys the uncertainty in the measurement.

- Usually, this means rounding off to the number of significant digits in in the quantity; that is, the number of digits (counting from the left) that are known exactly, plus one more.
- When this cannot be applied (as in the example above when addition of subtraction of the absolute uncertainty bridges a power of ten), then we round in such a way that the relative implied uncertainty in the result is as close as possible to that of the observed value.

Rounding the Results of Calculations

When carrying out calculations that involve multiple steps, you should avoid doing any rounding until you obtain the final result. Suppose you use your calculator to work out the area of a rectangle:



rounded value	relative implied uncertainty
1.58	1 part in 158, or 0.6%
1.6	1 part in 16, or 6 %

Note

Your calculator is of course correct as far as the pure numbers go, but you would be wrong to write down "1.57676 cm^2" as the answer. Two possible options for rounding off the calculator answer are shown at the right.

It is clear that neither option is entirely satisfactory; rounding to 3 significant digits overstates the precision of the answer, whereas following the rule and rounding to the two digits in ".42" has the effect of throwing away some precision. In this case, it could be argued that rounding to three digits is justified because the implied relative uncertainty in the answer, 0.6%, is more consistent with those of the two factors.

> *The "rules" for rounding off are generally useful, convenient guidelines, but they do not always yield the most desirable result. When in doubt, it is better to rely on relative implied uncertainties.*

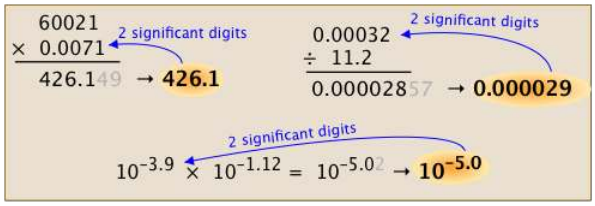
Addition and Subtraction

In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise that the least precise number used to get the answer. When adding or subtracting, we go by the number of *decimal places* (i.e., the number of digits on the right side of the decimal point) rather than by the number of significant digits. Identify the quantity having the smallest number of decimal places, and use this number to set the number of decimal places in the answer.



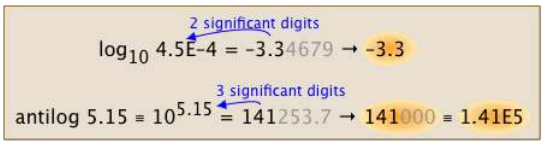
Multiplication and Division

The result must contain the same number of significant figures as in the value having the least number of significant figures.



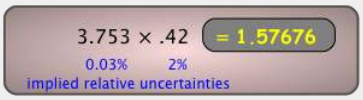
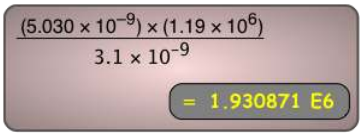
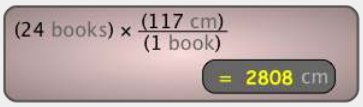
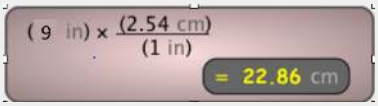
Logarithms and antilogarithms

If a number is expressed in the form $a \times 10^b$ ("scientific notation") with the additional restriction that the coefficient a is no less than 1 and less than 10, the number is in its *normalized* form. Express the base-10 logarithm of a value using the same number of significant figures as is present in the *normalized form* of that value. Similarly, for antilogarithms (numbers expressed as powers of 10), use the same number of significant figures as are in that power.

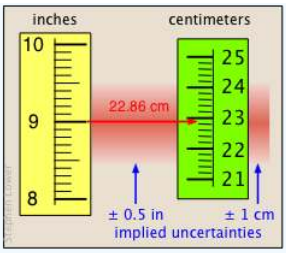


Examples 1.7.1

The following examples will illustrate the most common problems you are likely to encounter in rounding off the results of calculations. They deserve your careful study!

calculator result	rounded	remarks
	1.6	Rounding to two significant figures yields an implied uncertainty of 1/16 or 6%, three times greater than that in the least-precisely known factor. This is a good illustration of how rounding can lead to the loss of information.
	1.9E6	The "3.1" factor is specified to 1 part in 31, or 3%. In the answer 1.9, the value is expressed to 1 part in 19, or 5%. These precisions are comparable, so the rounding-off rule has given us a reasonable result.
A certain book has a thickness of 117 mm; find the height of a stack of 24 identical books: 	2810 mm	The “24” and the “1” are exact, so the only uncertain value is the thickness of each book, given to 3 significant digits. The trailing zero in the answer is only a placeholder.
	10.4	In addition or subtraction, look for the term having the smallest number of decimal places, and round off the answer to the same number of places.
		
	23 cm	see below

The last of the examples shown above represents the very common operation of converting one unit into another. There is a certain amount of ambiguity here; if we take "9 in" to mean a distance in the range 8.5 to 9.5 inches, then the implied uncertainty is ±0.5 in, which is 1 part in 18, or about ± 6%. The relative uncertainty in the answer must be the same, since all the values are multiplied by the same factor, 2.54 cm/in. In this case we are justified in writing the answer to two significant digits, yielding an uncertainty of about ±1 cm; if we had used the answer "20 cm" (one significant digit), its implied uncertainty would be ±5 cm, or ±25%.



When the appropriate number of significant digits is in question, calculating the relative uncertainty can help you decide.

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1.9: 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

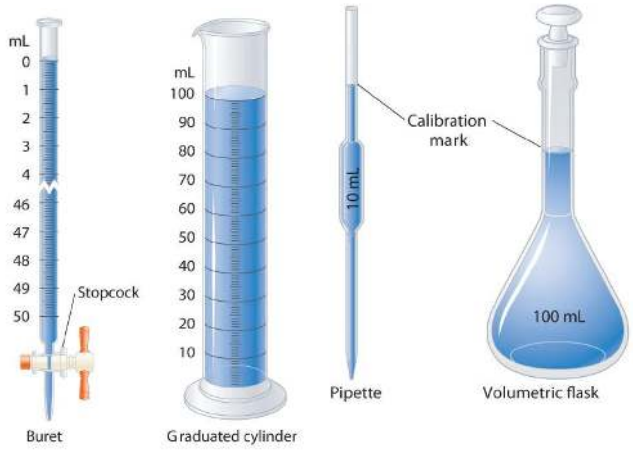


Figure* 1.9.1*: *(left) Graduated glassware is used to deliver variable volumes of liquid. (Right) Volumetric glassware is used to deliver (pipette) or contain (volumetric flask) a single volume accurately when filled to the calibration mark.*

A 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 (Figure 1.9.1), whereas we usually measure the mass of a solid or liquid substance with a balance (Figure 1.9.2). Measurements on an atomic or molecular scale, in contrast, require specialized instrumentation, such as the mass spectrometer described in Section 1.6.



Figure* 1.9.2: A balance is used to measure mass.*

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 1.9.1 lists the seven base units of the SI system; all other SI units of measurement are derived from them.

Table **1.9.1*:*** *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 1.9.2. To study chemistry, you need to know the information presented in Tables 1.9.1 and 1.9.2.

Table 1.9.2: *Prefixes Used with SI Units*

Prefix	Symbol	Value	Power of 10	Meaning
tera	T	1,000,000,000,000	10^{12}	trillion
giga	G	1,000,000,000	10^{9}	billion
mega	M	1,000,000	10^{6}	million
kilo	k	1000	10^{3}	thousand
hecto	h	100	10^{2}	hundred
deca	da	10	10^{1}	ten
—	—	1	10^{0}	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:

$$1L = 1000mL = 1dm^3 \tag{1.9.1}$$

$$1mL = 1cm^3 \tag{1.9.2}$$

$$1000cm^3 = 1L \tag{1.9.3}$$

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

$$N \times 10^{n} \tag{1.9.4}$$

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 Example 1.9.1.

Example 1.9.2

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

Explanation	Solution
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.	637.8 = 6.378×10^2.
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.	0.0479 = 4.79×10^{-2}.
this is usually expressed simply as 7.86. (Recall that $10^0 = 1$.)	7.86×10^0
because the decimal point was moved four places to the left, n = 4.	1.2378×10^4
because the decimal point was moved four places to the right, n = −4.	3.2×10^{-4}
this is usually expressed as 6.1067 × 10.	6.106700×10^1
	2.002080×10^3
	1.020×10^{-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. Example 1.9.2 illustrates how to do this.

Example 1.9.2

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

Explanation	Solution
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: In converting 48.66 × 10^2 to scientific notation, N has become more positive by 1 because the value of N has decreased.	$(1.36 \times 10^2) + (47.3 \times 10^2) = (1.36 + 47.3) \times 10^2 = 48.66 \times 10^2 = 4.87 \times 10^3$ $(0.136 \times 10^3) + (4.73 \times 10^3) = (0.136 + 4.73) \times 10^3 = 4.87 \times 10^3$

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 Example 1.9.3.

Example 1.9.3

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:

$$(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21} = 3.87 \times 10^{22} \quad (1.9.5)$$

b. In division, we subtract the exponents:

$$\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4} = 1.83 \times 10^{3} \quad (1.9.6)$$

c. This problem has both multiplication and division:

$$\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]} = 4.7 \times 10^{-31} \quad (1.9.7)$$

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:

$$1 ft = 12 in \quad (1.9.8)$$

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 8.00×10^{-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.

Example 1.9.4

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

Example 1.9.5

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 + 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.

Example 1.9.5

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. $(15.9994 \times 9) + 2.0158$

Solutions

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 Table 1.9.2.

Table 1.9.2: Three measurements from three balances

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:

$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}} \tag{1.9.9}$$

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

$$\text{deviation} = |\text{measurement} - \text{average}| \tag{1.9.10}$$

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:

$$\text{average} = \frac{\text{sum of deviations}}{\text{number of measurements}} \tag{1.9.11}$$

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

$$\frac{1.125\ g + 1.158\ g + 1.067\ g}{3} = 1.117\ g \tag{1.9.12}$$

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

$$\frac{0.008\ g + 0.041\ g + 0.050\ g}{3} = 0.033\ g \tag{1.9.13}$$

The precision of this set of measurements is therefore

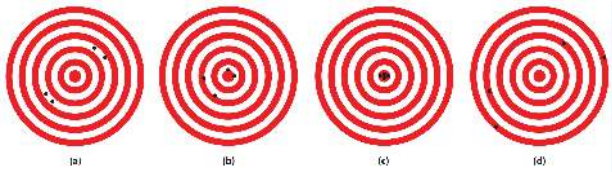
$$\frac{0.033\ g}{1.117\ g} \times 100 = 3.0\% \tag{1.9.14}$$

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 elsewhere.

Example 1.9.6

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)

Example 1.9.7

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

$$\frac{4.9mg}{457.3mg} \times 100 = 1.1\% \tag{1.9.15}$$

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.

$$\text{precision (Zn)} = \frac{0.2\%}{93.2\%} \times 100 = 0.2\% \tag{1.9.16}$$

$$\text{precision (Cu)} = \frac{0.2\%}{2.8\%} \times 100 = 7\% \tag{1.9.17}$$

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SECTION OVERVIEW

Unit I: Atomic Theory and Chemical Compounds

Chemistry is all around us "from the air we breathe to the food we eat" to the items at the super market that say “no chemicals added”. In fact, it is impossible to create something without using chemistry because chemistry consists of all matter. It allows us to answer questions as simple as why a candle goes out when a glass is placed over it to more complex questions such as does a candle actually burn in zero gravity? Chemistry is the study of matter and the changes it undergoes such as ice changing from the solid to liquid to gas phase. People have used it for things such as creating metal from an ore, dying fabric, and making cheese. Chemistry deals with different substances and how they can interact with each other to create a product.

2: Atoms and the Atomic Theory

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3: Chemical Compounds

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CHAPTER OVERVIEW

2: Atoms and the Atomic Theory



UC Davis CHE 2A: General Chemistry

Instructor: Gulacar

Chem 2A *Chem 2B* *Chem 2C*

Reading Assignments
Exercises
Worksheets
Homework

Unit I: Atomic Theory **Unit II: Chemical Reactions** **Unit III: Gases** **Unit IV: Electronic Structure and Bonding**

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In this chapter, you will learn how to describe the composition of chemical compounds. We introduce you to chemical nomenclature—the language of chemistry—that will enable you to recognize and name the most common kinds of compounds. An understanding of chemical nomenclature not only is essential for your study of chemistry but also has other benefits—for example, it helps you understand the labels on products found in the supermarket and the pharmacy. You will also be better equipped to understand many of the important environmental and medical issues that face society. By the end of this chapter, you will be able to describe what happens chemically when a doctor prepares a cast to stabilize a broken bone, and you will know the composition of common substances such as laundry bleach, the active ingredient in baking powder, and the foul-smelling compound responsible for the odor of spoiled fish. Finally, you will be able to explain the chemical differences among different grades of gasoline.

Topic hierarchy

2.1: Early Chemical Discoveries and Atomic Theory
2.2: Electrons and other Discoveries
2.3: The Nuclear Atom
2.4: Chemical Elements
2.5: Atomic Mass
2.6: Introduction to the Periodic Table
2.7: The Concept of Mole and the Avogadro Constant
2.8: The Mole and Molar Masses

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2.1: Early Chemical Discoveries and Atomic Theory

Learning Objectives

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.

Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC.

John Dalton (1766-1844) is the scientist credited for proposing the atomic theory. The theory explains several concepts that are relevant in the observable world: the composition of a pure gold necklace, what makes the pure gold necklace different than a pure silver necklace, and what occurs when pure gold is mixed with pure copper. This article explains the theories that Dalton used as a basis for his theory:

1. Law of Conservation of Mass
2. Law of Definite Proportions
3. Law of Multiple Proportions

Law 1: The Conservation of Mass

"Nothing comes from nothing" is an important idea in ancient Greek philosophy that argues that what exists **now** has always **existed**, since no new matter can come into existence where there was none before. Antoine Lavoisier (1743-1794) restated this principle for chemistry with the law of conservation of mass, which "means that the atoms of an object cannot be created or destroyed, but can be moved around and be changed into different particles." This law says that when a chemical reaction rearranges atoms into a new product, the mass of the reactants (chemicals before the chemical reaction) is the same as the mass of the products (the new chemicals made). More simply, whatever you do, you will still have the same amount of stuff (however, certain nuclear reactions like fusion and fission can convert a small part of the mass into energy.

The law of conservation of mass states that the total mass present before a chemical reaction is the same as the total mass present after the chemical reaction; in other words, **mass is conserved**. The law of conservation of mass was formulated by Lavoisier as a result of his combustion experiment, in which he observed that the mass of his original substance—a glass vessel, tin, and air—was equal to the mass of the produced substance—the glass vessel, “tin calx”, and the remaining air.

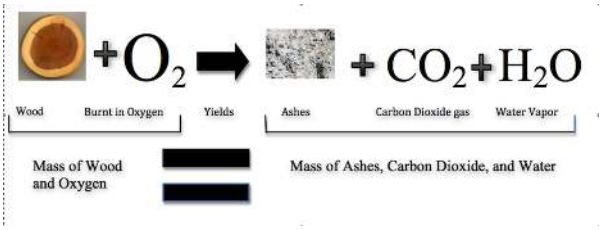


Figure 2.1.1: Image of the wood courtesy of Ehamberg and Stannered on Wikimedia Commons, available under Creative Commons Attribution 2.5 Generic license. Image of ashes courtesy of Walter Siegmund. Image as a whole constructed by Jessica Thornton (UCD).

Historically, this was a difficult concept for scientists to grasp. If this law was true, then how could a large piece of wood be reduced to a small pile of ashes? The wood clearly has a greater mass than the ashes. From this observation scientists concluded that mass had been lost. However, Figure 2.1.1 shows that the burning of word does follow the law of conservation of mass. Scientists did not account for the gases that play a critical role in this reaction.

Law 2: Definite Proportions

Joseph Proust (1754-1826) formulated the *law of definite proportions* (also called the **Law of Constant *Composition*** or **Proust's Law**). This law states that if a compound is broken down into its constituent elements, the masses of the constituents will always

have the same proportions, regardless of the quantity or source of the original substance. Joseph Proust based this law primarily on his experiments with basic copper carbonate. The illustration below depicts this law; 31 grams of H_2O and 8 grams of H_2O are made up of the same percent of hydrogen and oxygen.

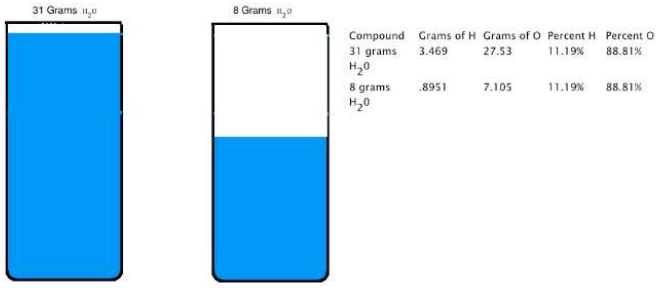


Figure 2.1.2: Constructed by Jessica Thornton (UCD)

Example 2.1.1: water

Oxygen makes up 88.8% of the mass of any sample of pure water, while hydrogen makes up the remaining 11.2% of the mass. You can get water by melting ice or snow, by condensing steam, from river, sea, pond, etc. It can be from different places: USA, UK, Australia, or anywhere. It can be made by chemical reactions like burning hydrogen in oxygen.

However, if the water is **pure**, it will **always** consist of 88.8 % oxygen by mass and 11.2 % hydrogen by mass, irrespective of its source or method of preparation.

Law 3: Multiple Proportions

Many combinations of elements can react to form more than one compound. In such cases, this law states that the weights of one element that combine with a fixed weight of another of these elements are integer multiples of one another. It's easy to say this, but please make sure that you understand how it works. Nitrogen forms a very large number of oxides, five of which are shown here.

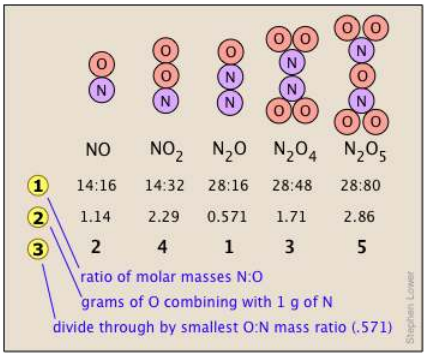


Figure 2.1.3: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds.

- Line 1 shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound. Thus for NO_2, we have (1 × 14) : (2 × 16) = 13:32. (These numbers were not known in the early days of Chemistry because atomic weights (i.e., molar masses) of most elements were not reliably known.)
- The numbers in Line 2 are just the mass ratios of O:N, found by dividing the corresponding ratios in line 1. But someone who depends solely on experiment would work these out by finding the mass of O that combines with unit mass (1 g) of nitrogen.
- Line is obtained by dividing the figures the previous line by the smallest O:N ratio in the line above, which is the one for N_2O. Note that just as the law of multiple proportions says, the weight of oxygen that combines with unit weight of nitrogen work out to small integers.
- Of course we just as easily could have illustrated the law by considering the mass of nitrogen that combines with one gram of oxygen; it works both ways!

The law of multiple proportions states that if two elements form more than one compound between them, the masses of one element combined with a fixed mass of the second element form in ratios of small integers.

Example 2.1.2: Oxides of Carbon

Consider two separate compounds are formed by only carbon and oxygen. The first compound contains 42.9% carbon and 57.1% oxygen (by mass) and the second compound contains 27.3% carbon and 72.7% oxygen (again by mass). Is this consistant with the law of multiple proportions?

Solution

The *Law of Multiple Proportions* states that the masses of one element which combine with a fixed mass of the second element are in a ratio of **whole** numbers. Hence, the masses of oxygen in the two compounds that combine with a fixed mass of carbon should be in a whole-number ratio.

Thus for every 1 g of the first compound there are 0.57 g of oxygen and 0.429 g of carbon. The mass of oxygen per gram carbon is:

$$\frac{0.571\ g\ oxygen}{0.429\ g\ carbon} = 1.33\ \frac{goxygen}{gcarbon} \tag{2.1.1}$$

Similarly, for 1 g of the second compound, there are 0.727 g oxygen and 0.273 g of carbon. The ration of mass of oxygen per gram of carbon is

$$\frac{0.727\ g\ oxygen}{0.273\ g\ carbon} = 2.66\ \frac{goxygen}{gcarbon} \tag{2.1.2}$$

Dividing the mass of oxygen per g of carbon of the second compound:

$$\frac{2.66}{1.33} = 2 \tag{2.1.3}$$

Hence the masses of oxygen combine with carbon in a 2:1 ratio which s consistent with the Law of Multiple Proportions since they are whole numbers.

Dalton's Atomic Theory

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 2.1.4), is a fundamental concept that states that all elements are composed of atoms. Previously, an atom was defined as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of the human pinkie (about 1 cm).

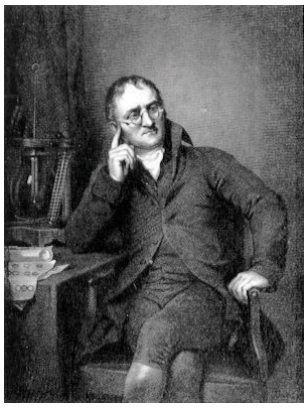


Figure 2.1.4 John Dalton was an English scientist who enunciated the modern atomic theory.

Dalton’s ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means “indivisible” or “uncuttable.”) Dalton had something that the ancient Greek philosophers didn’t have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study

nature. When Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Dalton's Theory was a powerful development as it explained the three laws of chemical combination (above) and recognized a workable distinction between the fundamental particle of an element (atom) and that of a compound (molecule). Six postulates are involved in Dalton's Atomic Theory:

1. All matter consists of indivisible particles called atoms.
2. Atoms of the same element are similar in shape and mass, but differ from the atoms of other elements.
3. Atoms cannot be created or destroyed.
4. Atoms of different elements may combine with each other in a fixed, simple, whole number ratios to form compound atoms.
5. Atoms of same element can combine in more than one ratio to form two or more compounds.
6. The atom is the smallest unit of matter that can take part in a chemical reaction.

In light of the current state of knowledge in the field of Chemistry, Dalton's theory had a few drawbacks. According to Dalton's postulates,

1. The indivisibility of an atom was proved wrong: an atom can be further subdivided into protons, neutrons and electrons. However an atom is the smallest particle that takes part in chemical reactions.
2. According to Dalton, the atoms of same element are similar in all respects. However, atoms of some elements vary in their masses and densities. These atoms of different masses are called isotopes. For example, chlorine has two isotopes with mass numbers 35 and 37.
3. Dalton also claimed that atoms of different elements are different in all respects. This has been proven wrong in certain cases: argon and calcium atoms each have an same atomic mass (40 amu).
4. According to Dalton, atoms of different elements combine in simple whole number ratios to form compounds. This is not observed in complex organic compounds like sugar ($C_{12}H_{22}O_{11}$).
5. The theory fails to explain the existence of allotropes (different forms of pure elements); it does not account for differences in properties of charcoal, graphite, diamond.

Despite these drawbacks, the importance of Dalton's theory should not be underestimated. He displayed exceptional insight into the nature of matter. and his ideas provided a framework that was later modified and expanded by other. Consequentially, John Dalton is often considered to be the father of modern atomic theory.



Fundamental Experiments in Chemistry: https://youtu.be/IhqqLGKmah4

References

1. Petrucci, Ralph, William Harwood, Geoffrey Herring, and Jeffry Madura. General Chemistry. 9th ed. Upper Saddle River, New Jersey: Pearson Prentince Hall, 2007
2. Moore, John. Chemistry for Dummies. John Wiley & Sons Inc, 2002.
3. Asimov, Isaac. A Short History of Chemistry. , CT.: Greenwood Press, 1965.
4. Patterson, Elizabeth C. John Dalton and the Atomic Theory. Garden City, NY: Doubleday, 1970
5. Myers, Richard. The Basics of Chemistry. Greenwood, 2003

6. Demtröder, Wolfgang. Atoms, Molecules and Photons: An Introduction to Atomic- Molecular- and Quantum Physics. 1st ed. Springer. 2002

Summary

This article explains the theories that Dalton used as a basis for his theory:

- Law of Conservation of Mass
- Law of Constant Composition
- Law of Multiple Proportions

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2.2: Electrons and other Discoveries

Learning Objectives

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

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 2.2.1). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the cathode, or negatively charged electrode; this form of energy was called a cathode ray.

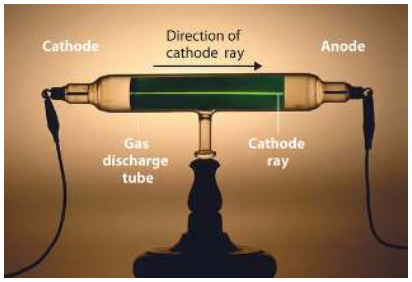


Figure 2.2.1: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light.

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic 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 2.2.2). 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; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

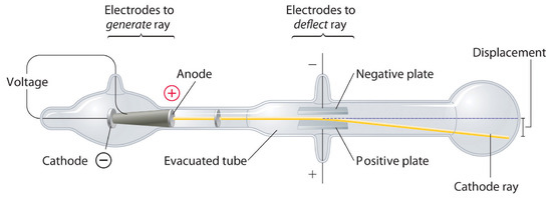


Figure 2.2.2: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged.

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:

$$\frac{mass}{charge} \times charge = mass \tag{2.2.1}$$

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy. The video below shows how JJ Thompson used such a tube to measure the ratio of charge over mass of an electron



Measuring e/m For an Electron. Video from Davidson College demonstrating Thompson's e/m experiment.

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.



Figure 2.2.3: 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.

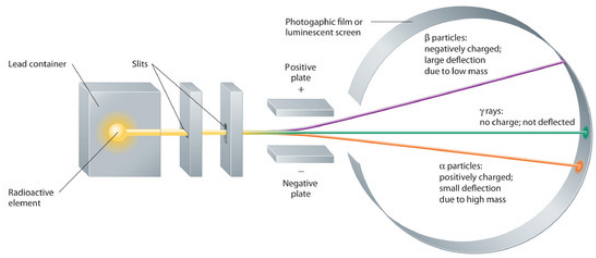


Figure 2.2.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.)

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 2.2.3 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 2.2.5 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.

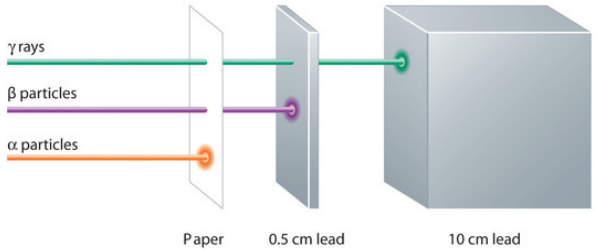


Figure 2.2.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them.

Summary

- Atoms are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of atoms and how they compose matter.

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).

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2.3: The Nuclear Atom

Learning Objectives

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

Dissecting the Atom

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 2.3.1).

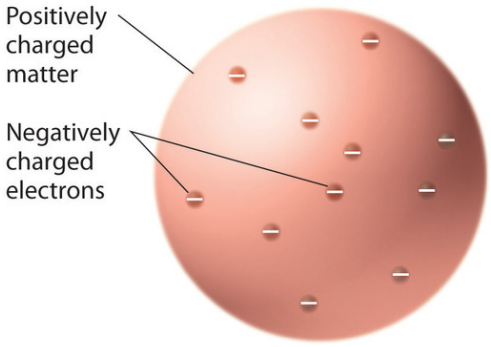


Figure 2.3.1: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge.

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (part (a) in Figure 2.3.2) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing 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 2.3.2). 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) in Figure 2.3.2). 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."

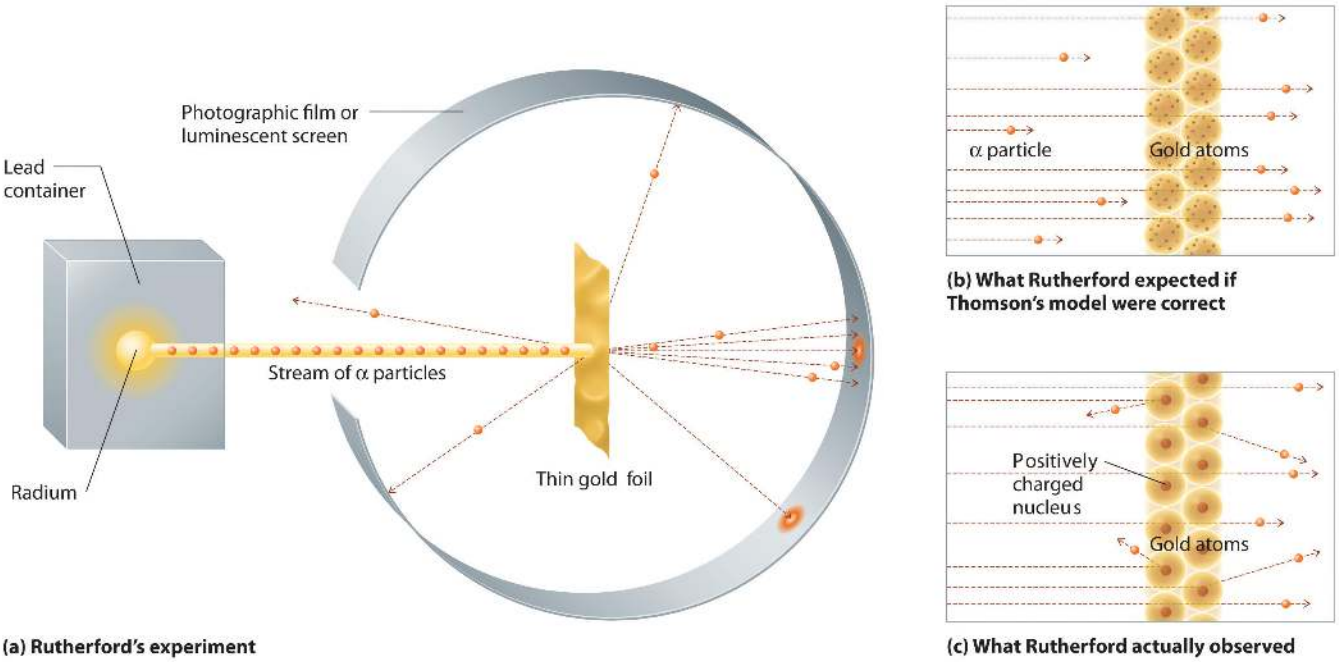


Figure 2.3.2: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, 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 it is known 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 considered physics superior to chemistry. In his opinion, "All science is either physics or stamp collecting."

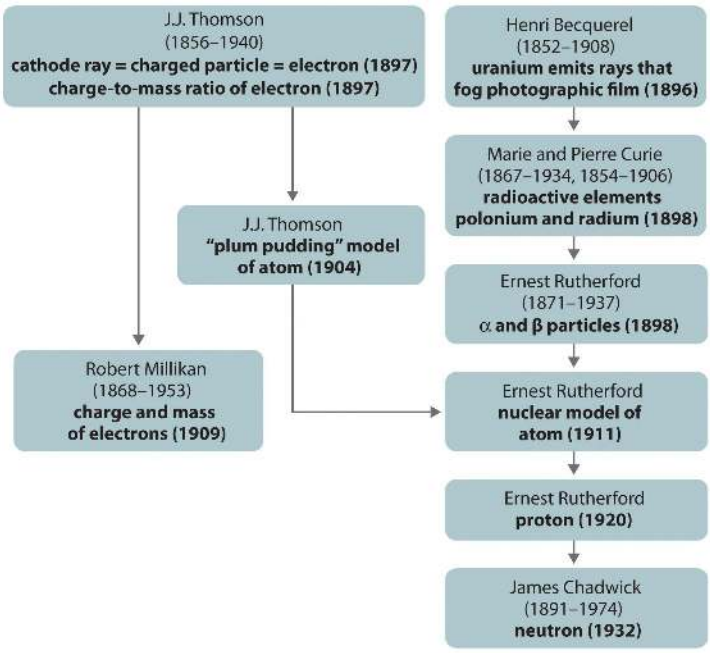


Figure 2.3.3: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed.

The historical development of the different models of the atom's structure is summarized in Figure 2.3.3. 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 the nucleus of a helium atom.

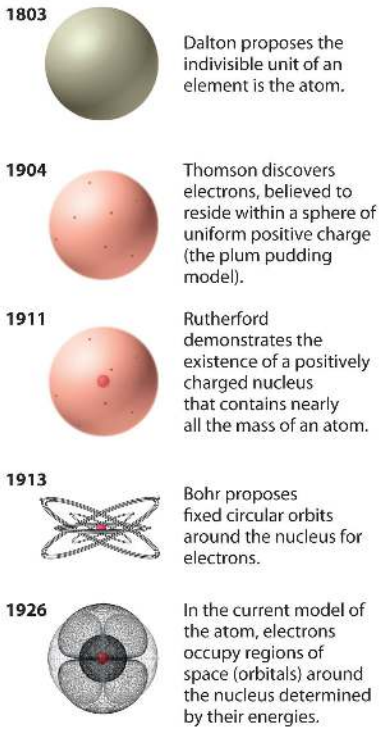


Figure 2.3.4: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms."

Rutherford's model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics. Figure 2.3.4 shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

The Nuclear Atom

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that

- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

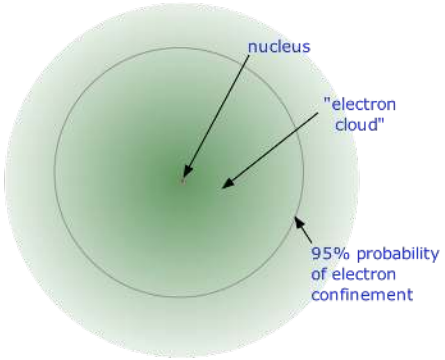


Figure 2.3.5: The structure of the nuclear atom with a central nucleus and surrounding electrons.

The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the *same* number of electrons outside the nucleus.

The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

Note

Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an *ion*.

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 discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 2.3.1 which illustrates three important points:

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. Relative charges of −1 and +1 are assigned 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 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 2.3.1: Properties of Subatomic Particles*

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

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



The Nuclear Atom: https://youtu.be/eqoyZuv1tWA

Summary

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

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).

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?

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 1.3 and the periodic table (see Chapter 32), calculate the percentage of the mass of a silicon atom that is due to

a. electrons.

b. protons.

2. Using the data in Table 1.3 and the periodic table (see Chapter 32), calculate the percentage of the mass of a helium atom that is due to

    a. electrons.

    b. 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 3.84×10^{-18} coulombs. What is the total number of electrons contained in the drop?

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2.4: Chemical Elements

Learning Objectives

- To know the meaning of isotopes and atomic masses.

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. 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 indicate 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 2.4.1.

Table 2.4.1: 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

Atomic Number (Z)

What single parameter uniquely characterizes the atom of a given element? It is not the atom's relative mass, as we will see in the section on isotopes below. It is, rather, the number of protons in the nucleus, which we call the *atomic number* and denote by the symbol *Z*. Each proton carries an electric charge of +1, so the atomic number also specifies the electric charge of the nucleus. In the neutral atom, the *Z protons* within the nucleus are balanced by *Z electrons* outside it.

Henry Moseley

Atomic numbers were first worked out in 1913 by Henry Moseley, a young member of Rutherford's research group in Manchester. Moseley searched for a measurable property of each element that increases linearly with atomic number. He found this in a class of X-rays emitted by an element when it is bombarded with electrons. The frequencies of these X-rays are unique

to each element, and they increase uniformly in successive elements. Moseley found that the square roots of these frequencies give a straight line when plotted against Z; this enabled him to sort the elements in order of increasing atomic number.



You can think of the atomic number as a kind of serial number of an element, commencing at 1 for hydrogen and increasing by one for each successive element. The chemical name of the element and its symbol are uniquely tied to the atomic number; thus the symbol "Sr" stands for strontium, whose atoms all have $Z = 38$.

Mass number (A)

This is just the sum of the numbers of protons and neutrons in the nucleus. It is sometimes represented by the symbol *A*, so

$$A = Z + N \tag{2.4.1}$$

in which *Z* is the atomic number and *N* is the *neutron number*.

Nuclides and their Symbols

The term *nuclide* simply refers to any particular kind of nucleus. For example, a nucleus of atomic number 7 is a nuclide of nitrogen. Any nuclide is characterized by the pair of numbers (*Z* ,*A*). The element symbol depends on *Z* alone, so the symbol ^{26}Mg is used to specify the mass-26 nuclide of manganese, whose name implies *Z*=12. A more explicit way of denoting a particular kind of nucleus is to add the atomic number as a subscript. Of course, this is somewhat redundant, since the symbol Mg **always** implies *Z*=12, but it is sometimes a convenience when discussing several nuclides.

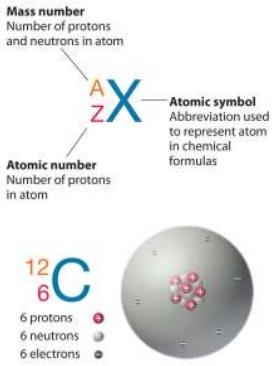


Figure 2.4.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

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 ${}^{A}_{Z}X$, where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore ${}^{12}_{6}C$. The subscript indicating the atomic number is actually **redundant** because the atomic symbol already uniquely specifies Z. Consequently, ${}^{12}_{6}C$ 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.

Isotopes

Recall 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.

Two nuclides having the **same** atomic number but different mass numbers are known as *isotopes*. Most elements occur in nature as mixtures of isotopes, but twenty-three of them (including beryllium and fluorine, shown in the table) are monoisotopic. For example, there are three *natural isotopes* of magnesium: ^{24}Mg (79% of all Mg atoms), ^{25}Mg (10%), and ^{26}Mg (11%); all three are present in all compounds of magnesium in about these same proportions.

	Z	mass numbers
H	1	1 2 3
He	2	3 4
Li	3	6 7
Be	4	9
B	5	10 11
C	6	12 13 14
N	7	14 15
O	8	16 17 18
F	9	19
Ne	10	20 21 22

Approximately 290 isotopes occur in nature. The two heavy isotopes of hydrogen are especially important— so much so that they have names and symbols of their own:

$$\underset{\text{protium}}{{}^{1}_{1}\mathrm{H}} \tag{2.4.2}$$

$$\underset{\text{deuterium}}{{}^{2}_{1}\mathrm{H} \equiv \mathrm{D}} \tag{2.4.3}$$

$$\underset{\text{tritium}}{{}^{2}_{1}\mathrm{H} \equiv \mathrm{T}} \tag{2.4.4}$$

Deuterium accounts for only about 15 out of every one million atoms of hydrogen. Tritium, which is radioactive, is even less abundant. All the tritium on the earth is a by-product of the decay of other radioactive elements.

For carbon, in addition to ^{12}C, a typical sample of carbon contains 1.11% $^{13}_{6}C$ (^{13}C), with 7 neutrons and 6 protons, and a trace of $^{14}_{6}C$ (^{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 archeology. 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 2.4.2.

Table 2.4.2: 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

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
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.



How Elements Are Represented on the Periodic Table: https://youtu.be/ik6ZsaSyISo

Example 2.4.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A. Refer to the periodic table 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 ${}^{206}_{82}Pb$, ${}^{207}_{82}Pb$, and ${}^{208}_{82}Pb$, which are usually abbreviated as ${}^{206}Pb$, ${}^{207}Pb$, and ${}^{208}Pb$.

Exercise 2.4.1

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

Answer: ${}^{79}_{35}\mathrm{Br}$ and ${}^{81}_{35}\mathrm{Br}$ or, more commonly, ${}^{79}\mathrm{Br}$ and ${}^{81}\mathrm{Br}$.

Summary

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

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.

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2.5: Atomic Mass

Learning Objectives

- to know the meaning of isotopes and atomic masses.

Atomic and Molecular Weights

The subscripts in chemical formulas, and the coefficients in chemical equations represent *exact* quantities. H_2O, for example, indicates that a water molecule comprises exactly **two** atoms of hydrogen and **one** atom of oxygen. The following equation:

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l) \tag{2.5.1}$$

not only tells us that propane reacts with oxygen to produce carbon dioxide and water, but that ***1*** molecule of propane reacts with ***5*** molecules of oxygen to produce ***3*** molecules of carbon dioxide and ***4*** molecules of water. Since counting individual atoms or molecules is a little difficult, quantitative aspects of chemistry rely on knowing the *masses* of the compounds involved.

Atoms of different elements have different masses. Early work on the separation of water into its constituent elements (hydrogen and oxygen) indicated that 100 grams of water contained 11.1 grams of hydrogen and 88.9 grams of oxygen:

$$100\ \text{grams Water} \rightarrow 11.1\ \text{grams Hydrogen} + 88.9\ \text{grams Oxygen} \tag{2.5.2}$$

Later, scientists discovered that water was composed of ***two atoms*** of hydrogen ***for each atom*** of oxygen. Therefore, in the above analysis, *in the 11.1 grams of hydrogen there were twice as many atoms as in the 88.9 grams of oxygen.* Therefore, an oxygen atom must weigh about 16 times as much as a hydrogen atom:

$$\frac{\frac{88.9\ g\ Oxygen}{1\ atom}}{\frac{111\ g\ Hydrogen}{2\ atoms}} = 16 \tag{2.5.3}$$

Hydrogen, the lightest element, was assigned a relative mass of '1', and the other elements were assigned 'atomic masses' relative to this value for hydrogen. Thus, oxygen was assigned an atomic mass of 16. We now know that a **hydrogen** atom has a mass of **1.6735 x 10^{-24}** grams, and that the **oxygen** atom has a mass of **2.6561 X 10^{-23}** grams. As we saw earlier, it is convenient to use a reference unit when dealing with such small numbers: the **atomic mass unit**. The atomic mass unit (***amu***) was not standardized against hydrogen, but rather, against the ^{12}C isotope of **carbon** (***amu* = 12**).

Thus, the mass of the **hydrogen atom** (^{1}H) is 1.0080 *amu*, and the mass of **an oxygen atom** (^{16}O) is 15.995 *amu*. Once the masses of atoms were determined, the ***amu*** could be assigned an actual value:

1 ***amu*** = 1.66054 x 10^{-24} **grams** conversely: 1 **gram** = 6.02214 x 10^{23} ***amu***

Average Atomic Mass

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision (Table 2.3.1), 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.

Because atoms are much too small to measure individually and do not have charges, 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 2.5.1). 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.

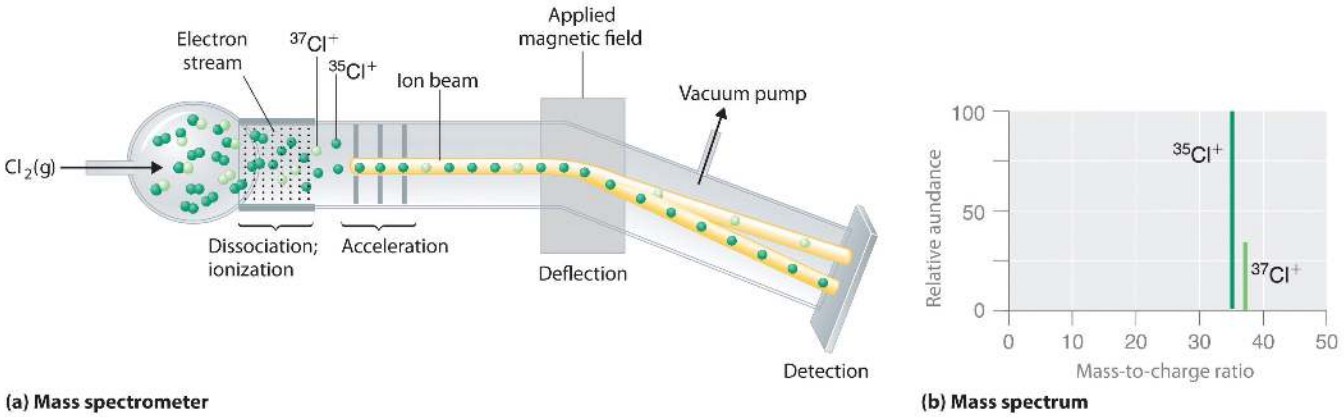


Figure 2.5.1: Determining Relative Atomic Masses Using a Mass Spectrometer. Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules 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 or u), 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 2.3.2 whose exact atomic mass is equal to the mass number. Experiments have shown that 1 amu = 1.66×10^{-24} g.

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

$$\frac{\text{mass of } ^2\text{H}}{\text{mass of } ^{12}\text{C}} \times \text{mass of } ^{12}\text{C} = 0.167842 \times 12 \text{ amu} = 2.104104 \text{ amu} \tag{2.5.4}$$

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

The periodic table lists the atomic masses of all the elements. Comparing these values with those given for some of the isotopes in Table 2.3.2 reveals 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 follows:

$$(0.9889 \times 12 \text{ amu}) + (0.0111 \times 13.003355 \text{ amu}) = 12.01 \text{ amu} \tag{2.5.5}$$

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



Finding the Averaged Atomic Weight of an Element: https://youtu.be/bmP6Gr9zJiQ

Example 2.5.1: Bromine

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

$$^{79}\text{Br}: \frac{50.69}{100} = 0.5069 \tag{2.5.6}$$

$$^{81}\text{Br}: \frac{49.31}{100} = 0.4931 \tag{2.5.7}$$

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

$$^{79}\text{Br}: 79.9183\ amu \times 0.5069 = 40.00\ amu$$

$$^{81}\text{Br}: 80.9163\ amu \times 0.4931 = 39.90\ amu$$

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 2.5.1

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

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. Each atom of an element contains the same number of protons, known as 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.

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2.6: Introduction to the Periodic Table

Learning Objectives

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

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 2.6.1). The rationale for the peculiar format of the periodic table is explained later. 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.

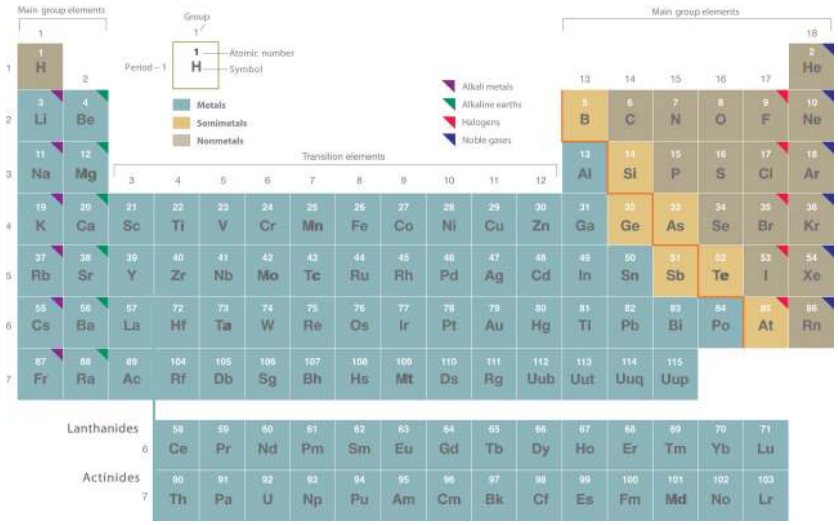


Figure 2.6.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals.

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 facilitates the prediction of 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.

Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in Figure 2.6.1 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). Gold-colored lements 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 2.6.1

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

Given: element

Asked for: classification

Strategy:

Find selenium in the periodic table shown in Figure 2.6.1 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 Figure 2.6.1, 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 2.6.1

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 previously 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.

Group 1: 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.

Group 2: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are 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.

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words 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.

Group 18: 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 called 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 noble gases are unreactive at room temperature and pressure.



Periodic Law in the Periodic Table: https://youtu.be/ciJYvhRF5i4

Summary

- The periodic table is used as a predictive tool.

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.

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2.7: The Concept of Mole and the Avogadro Constant

$$2 \times \text{ atomic mass of carbon} = 2\,atoms\left(\frac{12.011\,amu}{atoms}\right) = 24.022\,amu \tag{2.7.1}$$

$$6 \times \text{ atomic mass of hydrogen} = 2\,atoms\left(\frac{1.0079\,amu}{atoms}\right) = 6.0474\,amu \tag{2.7.2}$$

$$1 \times \text{ atomic mass of oxygen} = 1\,atoms\left(\frac{15.9994\,amu}{atoms}\right) = 15.994\,amu \tag{2.7.3}$$

C Adding together the masses gives the molecular mass:

$$24.022\,amu + 6.0474\,amu + 15.9994\,amu = 46.069\,amu \tag{2.7.4}$$

Alternatively, we could have used unit conversions to reach the result in one step:

$$\left[2\,atoms C\left(\frac{12.011\,amu}{1\,atom C}\right)\right] + \left[6\,atoms H\left(\frac{1.0079\,amu}{1\,atom H}\right)\right] + \left[1\,atoms C\left(\frac{15.9994\,amu}{1\,atom 0}\right)\right] = 46.069\,amu \tag{2.7.5}$$

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

$$2C \quad (2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{2.7.6}$$

$$6H \quad (6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{2.7.7}$$

$$+1O \quad (1\,atoms)(15.9994\,amu/atom) = 15.9994\,amu \tag{2.7.8}$$

$$C_2H_6O \quad \text{molecular mass of ethanol} = 46.069\,amu \tag{2.7.9}$$

? Exercise 2.7.1: Molecular Mass of Freon

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 form covalent bonds, ionic compounds do not have a readily identifiable molecular unit. Therefore, for ionic compounds, the formula mass (also called the empirical formula mass) of the compound is used instead of 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. The units are atomic mass units.

Note

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



Determining the Molar Mass of a Molecule: https://youtu.be/wOjQjZqX7l8

Example 2.7.2: Formula Mass of Calcium Phosphate

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

$$3 \times \text{atomic mass of calcium} = 3\ atoms\left(\frac{40.078\ amu}{atom}\right) = 120.234\ amu \tag{2.7.10}$$

$$2 \times \text{atomic mass of phosphorus} = 2\ atoms\left(\frac{30.973761\ amu}{atom}\right) = 61.947522\ amu \tag{2.7.11}$$

$$8 \times \text{atomic mass of oxygen} = 8\ atoms\left(\frac{15.9994\ amu}{atom}\right) = 127.9952\ amu \tag{2.7.12}$$

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

$$120.234\ amu + 61.947522\ amu + 127.9952\ amu = 310.177\ amu \tag{2.7.13}$$

We could also find the formula mass of Ca3(PO4)2 in one step by using unit conversions or a tabular format:

$$\left[3\ atoms Ca\left(\frac{40.078\ amu}{1\ atom Ca}\right)\right] + \left[2\ atoms P\left(\frac{30.973761\ amu}{1\ atom P}\right)\right] + \left[8\ atoms O\left(\frac{15.9994\ amu}{1\ atom O}\right)\right] \tag{2.7.14}$$

$$= 310.177\ amu \tag{2.7.15}$$

$$3Ca \quad (3\ atoms)(40.078\ amu/atom) = 120.234\ amu \tag{2.7.16}$$

$$2P \quad (2\ atoms)(30.973761\ amu/atom) = 61.947522\ amu \tag{2.7.17}$$

$$+8O \quad (8\,atoms)(15.9994\,amu/atom) = 127.9952\,amu \tag{2.7.18}$$

$$Ca_3P_2O_8 \quad \text{formula mass of } Ca_3(PO_4)_2 = 310.177\,amu \tag{2.7.19}$$

$$(moles)(molarmass) \rightarrow mass \tag{2.7.20}$$

or, more specifically,

$$moles\left(\frac{grams}{mole}\right) = grams \tag{2.7.21}$$

Conversely, to convert the mass of a substance to moles:

$$\left(\frac{grams}{molarmass}\right) \rightarrow moles \tag{2.7.22}$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles \tag{2.7.23}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{2.7.24}$$

the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2. Therefore, when considering ***this*** particular reaction

- **2 moles** of H_2
- **1 mole** of O_2 and
- **2 moles** of H_2O

would be considered to be ***stoichiometrically equivalent quantitites***.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{2.7.25}$$

The ratio $\left(\frac{2\ mol\ H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

Example 2.7.3

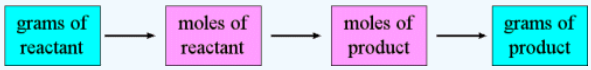
For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{2.7.26}$$

Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10}.

Solution

Thus, the overall sequence of steps to solve this problem is:



First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{2.7.27}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{2.7.28}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{2.7.29}$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2}\ mol\ CO_2 \left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2} \right) = 3.03\ g\ CO_2 \tag{2.7.30}$$

Be sure to pay attention to the units when converting between mass and moles. Figure 2.7.1 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 2.7.3 and Example 2.7.4.

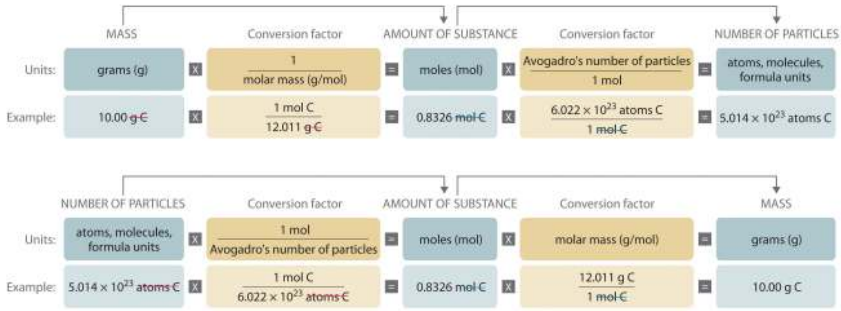


Figure 2.7.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units



Conversions Between Grams, Mol, & Atoms: https://youtu.be/rOvErpAnoCg

Example 2.7.4

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

a. moles.
b. 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:

a. **A** The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 2.7.2.7.1:

$$2C(2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{2.7.31}$$

$$6H(6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{2.7.32}$$

$$2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{2.7.33}$$

$$C_2H_6O_2\text{molecular mass of ethylene glycol} = 62.068\,amu \tag{2.7.34}$$

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

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):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)} \tag{2.7.35}$$

So

$$35.00\,g\text{ethylene glycol}\left(\frac{1\,mole\text{ethylene glycol}}{62.068\,g\text{ethylene glycol}}\right) = 0.5639\,mol\text{ethylene glycol} \tag{2.7.36}$$

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.

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

$$\text{molecules of ethylene glycol} = 0.5639\,mol\left(\frac{6.022\times10^{23}\,molecules}{1\,mol}\right) \tag{2.7.37}$$

$$= 3.396\times10^{23}\,molecules \tag{2.7.38}$$

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 × 10^{23} molecules, which is indeed the case.

$$2S(2\,atoms)(32.065\,amu/atom) = 64.130\,amu \tag{2.7.39}$$

$$+2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu \tag{2.7.40}$$

$$S_2Cl_2\text{molecular mass of } S_2Cl_2 = 135.036\,amu \tag{2.7.41}$$

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:

$$moles S_2Cl_2\left[\text{molar mass}\left(\frac{g}{mol}\right)\right] \rightarrow mass of\,S_2Cl_2\,(g) \tag{2.7.42}$$

$$1.75\,molS_2Cl_2\left(\frac{135.036\,gS_2Cl_2}{1\,molS_2Cl_2}\right) = 236\,gS_2Cl_2 \tag{2.7.43}$$

b.

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

$$1Ca(1\,atom)(40.078\,amu/atom) = 40.078\,amu \tag{2.7.44}$$

$$2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu \tag{2.7.45}$$

$$+2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{2.7.46}$$

$$Ca(ClO)_2\text{ formula mass of } Ca(ClO)_2 = 142.983\,amu \tag{2.7.47}$$

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:

$$moles Ca(ClO)_2\left[\frac{\text{molar mass}Ca(ClO)_2}{1\,molCa(ClO)_2}\right] = mass Ca(ClO)_2 \tag{2.7.48}$$

$$1.75\ mol Ca(ClO)_2 \left[\frac{142.983\ g Ca(ClO)_2}{1\ mol Ca(ClO)_2}\right] = 250\ g Ca(ClO)_2 \tag{2.7.49}$$

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 2.7.5

Calculate the mass of 0.0122 mol of each compound.

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

Answer:

a. 1.71 g
b. 0.721 g

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative number of moles. For example, in the *balanced* equation:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{2.7.50}$$

the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2. Therefore, when considering ***this*** particular reaction

- **2 moles** of H_2
- **1 mole** of O_2 and
- **2 moles** of H_2O

would be considered to be ***stoichiometrically equivalent quantitites***.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{2.7.51}$$

The ratio $\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

✓ Example 2.7.6

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{2.7.52}$$

Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10}.

Solution

First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{2.7.53}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{2.7.54}$$

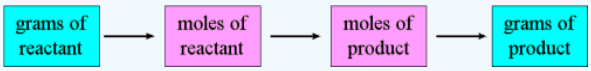
Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{2.7.55}$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2}\ mol\ CO_2 \left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2} \right) = 3.03\ g\ CO_2 \tag{2.7.56}$$

Thus, the overall sequence of steps to solve this problem were:



In a similar way we could determine the mass of water produced, or oxygen consumed, etc.

Summary

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

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, Avogadro's number (6.022×10^{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 6.022×10^{23} atoms, molecules, or formula units of that substance.

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2.8: The Mole and Molar Masses

$$2 \times \text{ atomic mass of carbon} = 2\,atoms\left(\frac{12.011\,amu}{atoms}\right) = 24.022\,amu \tag{2.8.1}$$

$$6 \times \text{ atomic mass of hydrogen} = 2\,atoms\left(\frac{1.0079\,amu}{atoms}\right) = 6.0474\,amu \tag{2.8.2}$$

$$1 \times \text{ atomic mass of oxygen} = 1\,atoms\left(\frac{15.9994\,amu}{atoms}\right) = 15.994\,amu \tag{2.8.3}$$

C Adding together the masses gives the molecular mass:

$$24.022\,amu + 6.0474\,amu + 15.9994\,amu = 46.069\,amu \tag{2.8.4}$$

Alternatively, we could have used unit conversions to reach the result in one step:

$$\left[2\,atoms C\left(\frac{12.011\,amu}{1\,atom C}\right)\right] + \left[6\,atoms H\left(\frac{1.0079\,amu}{1\,atom H}\right)\right] + \left[1\,atoms C\left(\frac{15.9994\,amu}{1\,atom 0}\right)\right] = 46.069\,amu \tag{2.8.5}$$

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

$$2C \quad (2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{2.8.6}$$

$$6H \quad (6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{2.8.7}$$

$$+1O \quad (1\,atoms)(15.9994\,amu/atom) = 15.9994\,amu \tag{2.8.8}$$

$$C_2H_6O \quad \text{molecular mass of ethanol} = 46.069\,amu \tag{2.8.9}$$

? Exercise 2.8.1: Molecular Mass of Freon

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 form covalent bonds, ionic compounds do not have a readily identifiable molecular unit. Therefore, for ionic compounds, the formula mass (also called the empirical formula mass) of the compound is used instead of 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. The units are atomic mass units.

Note

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



Determining the Molar Mass of a Molecule: https://youtu.be/wOjQjZqX7l8

Example 2.8.2: Formula Mass of Calcium Phosphate

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

$$3 \times \text{atomic mass of calcium} = 3\ atoms\left(\frac{40.078\ amu}{atom}\right) = 120.234\ amu \tag{2.8.10}$$

$$2 \times \text{atomic mass of phosphorus} = 2\ atoms\left(\frac{30.973761\ amu}{atom}\right) = 61.947522\ amu \tag{2.8.11}$$

$$8 \times \text{atomic mass of oxygen} = 8\ atoms\left(\frac{15.9994\ amu}{atom}\right) = 127.9952\ amu \tag{2.8.12}$$

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

$$120.234\ amu + 61.947522\ amu + 127.9952\ amu = 310.177\ amu \tag{2.8.13}$$

We could also find the formula mass of Ca3(PO4)2 in one step by using unit conversions or a tabular format:

$$\left[3\ atoms Ca\left(\frac{40.078\ amu}{1\ atom Ca}\right)\right] + \left[2\ atoms P\left(\frac{30.973761\ amu}{1\ atom P}\right)\right] + \left[8\ atoms O\left(\frac{15.9994\ amu}{1\ atom O}\right)\right] \tag{2.8.14}$$

$$= 310.177\ amu \tag{2.8.15}$$

$$3Ca \quad (3\ atoms)(40.078\ amu/atom) = 120.234\ amu \tag{2.8.16}$$

$$2P \quad (2\ atoms)(30.973761\ amu/atom) = 61.947522\ amu \tag{2.8.17}$$

$$+8O \quad (8\,atoms)(15.9994\,amu/atom) = 127.9952\,amu \tag{2.8.18}$$

$$Ca_3P_2O_8 \quad \text{formula mass of } Ca_3(PO_4)_2 = 310.177\,amu \tag{2.8.19}$$

$$(moles)(molarmass) \rightarrow mass \tag{2.8.20}$$

or, more specifically,

$$moles\left(\frac{grams}{mole}\right) = grams \tag{2.8.21}$$

Conversely, to convert the mass of a substance to moles:

$$\left(\frac{grams}{molarmass}\right) \rightarrow moles \tag{2.8.22}$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles \tag{2.8.23}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{2.8.24}$$

the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2. Therefore, when considering ***this*** particular reaction

- **2 moles** of H_2
- **1 mole** of O_2 and
- **2 moles** of H_2O

would be considered to be ***stoichiometrically equivalent quantitites***.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{2.8.25}$$

The ratio $\left(\frac{2\ mol\ H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

Example 2.8.3

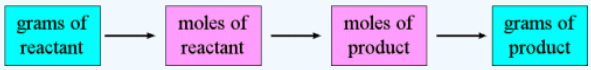
For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{2.8.26}$$

Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10}.

Solution

Thus, the overall sequence of steps to solve this problem is:



First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{2.8.27}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{2.8.28}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{2.8.29}$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2}\ mol\ CO_2 \left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2} \right) = 3.03\ g\ CO_2 \tag{2.8.30}$$

Be sure to pay attention to the units when converting between mass and moles. Figure 2.8.1 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 2.8.3 and Example 2.8.4.

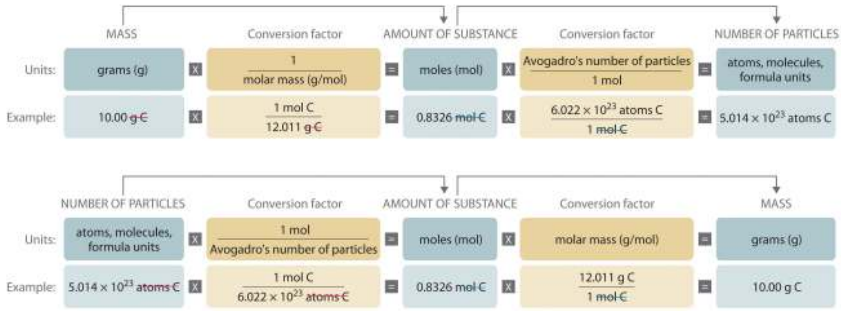


Figure 2.8.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units



Conversions Between Grams, Mol, & Atoms: https://youtu.be/rOvErpAnoCg

Example 2.8.4

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

a. moles.
b. 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:

a. **A** The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 2.8.2.7.1:

$$2C(2\,atoms)(12.011\,amu/atom) = 24.022\,amu \tag{2.8.31}$$

$$6H(6\,atoms)(1.0079\,amu/atom) = 6.0474\,amu \tag{2.8.32}$$

$$2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{2.8.33}$$

$$C_2H_6O_2\text{molecular mass of ethylene glycol} = 62.068\,amu \tag{2.8.34}$$

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

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):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)} \tag{2.8.35}$$

So

$$35.00\,g\text{ethylene glycol}\left(\frac{1\,mole\text{ethylene glycol}}{62.068\,g\text{ethylene glycol}}\right) = 0.5639\,mol\text{ethylene glycol} \tag{2.8.36}$$

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.

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

$$\text{molecules of ethylene glycol} = 0.5639\,mol\left(\frac{6.022\times10^{23}\,molecules}{1\,mol}\right) \tag{2.8.37}$$

$$= 3.396\times10^{23}\,molecules \tag{2.8.38}$$

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 × 10^{23} molecules, which is indeed the case.

$$2S(2\,atoms)(32.065\,amu/atom) = 64.130\,amu \tag{2.8.39}$$

$$+2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu \tag{2.8.40}$$

$$S_2Cl_2\text{molecular mass of } S_2Cl_2 = 135.036\,amu \tag{2.8.41}$$

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:

$$moles S_2Cl_2\left[\text{molar mass}\left(\frac{g}{mol}\right)\right] \rightarrow mass of\,S_2Cl_2\,(g) \tag{2.8.42}$$

$$1.75\,molS_2Cl_2\left(\frac{135.036\,gS_2Cl_2}{1\,molS_2Cl_2}\right) = 236\,gS_2Cl_2 \tag{2.8.43}$$

b.

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

$$1Ca(1\,atom)(40.078\,amu/atom) = 40.078\,amu \tag{2.8.44}$$

$$2Cl(2\,atoms)(35.453\,amu/atom) = 70.906\,amu \tag{2.8.45}$$

$$+2O(2\,atoms)(15.9994\,amu/atom) = 31.9988\,amu \tag{2.8.46}$$

$$Ca(ClO)_2\text{ formula mass of } Ca(ClO)_2 = 142.983\,amu \tag{2.8.47}$$

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:

$$moles Ca(ClO)_2\left[\frac{\text{molar mass}Ca(ClO)_2}{1\,molCa(ClO)_2}\right] = mass Ca(ClO)_2 \tag{2.8.48}$$

$$1.75\ mol Ca(ClO)_2 \left[\frac{142.983\ g Ca(ClO)_2}{1\ mol Ca(ClO)_2}\right] = 250\ g Ca(ClO)_2 \tag{2.8.49}$$

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 2.8.5

Calculate the mass of 0.0122 mol of each compound.

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

Answer:

a. 1.71 g
b. 0.721 g

The coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative number of moles. For example, in the *balanced* equation:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \tag{2.8.50}$$

the production of two moles of water would require the consumption of 2 moles of H_2 and one mole of O_2. Therefore, when considering ***this*** particular reaction

- **2 moles** of H_2
- **1 mole** of O_2 and
- **2 moles** of H_2O

would be considered to be ***stoichiometrically equivalent quantitites***.

These stoichiometric relationships, derived from balanced equations, can be used to determine expected amounts of products given amounts of reactants. For example, how many moles of H_2O would be produced from 1.57 moles of O_2?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{2.8.51}$$

The ratio $\left(\frac{2\ mol\backslash l H_2O}{1\ mol\ O_2}\right)$ is the stoichiometric relationship between H_2O and O_2 from the balanced equation for this reaction.

✓ Example 2.8.6

For the combustion of butane (C_4H_{10}) the balanced equation is:

$$2C_4H_{10(l)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)} \tag{2.8.52}$$

Calculate the mass of CO_2 that is produced in burning 1.00 gram of C_4H_{10}.

Solution

First of all we need to calculate how many moles of butane we have in a 1.00 gram sample:

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{2.8.53}$$

Now, the stoichiometric relationship between C_4H_{10} and CO_2 is:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{2.8.54}$$

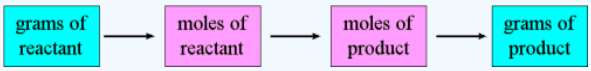
Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{2.8.55}$$

The question called for the determination of the mass of CO_2 produced, thus we have to convert moles of CO_2 into grams (by using the **molecular weight** of CO_2):

$$6.88 \times 10^{-2}\ mol\ CO_2 \left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2} \right) = 3.03\ g\ CO_2 \tag{2.8.56}$$

Thus, the overall sequence of steps to solve this problem were:



In a similar way we could determine the mass of water produced, or oxygen consumed, etc.

Summary

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

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, Avogadro's number (6.022×10^{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 6.022×10^{23} atoms, molecules, or formula units of that substance.

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CHAPTER OVERVIEW

3: Chemical Compounds



UC Davis CHE 2A: General Chemistry

Instructor: Gulacar

Chem 2A *Chem 2B* *Chem 2C*

Reading Assignments
Exercises
Worksheets
Homework

Unit I: Atomic Theory **Unit II: Chemical Reactions** **Unit III: Gases** **Unit IV: Electronic Structure and Bonding**

Template:HideTOC

We begin this chapter by describing the relationship between the mass of a sample of a substance and its composition. We then develop methods for determining the quantities of compounds produced or consumed in chemical reactions, and we describe some fundamental types of chemical reactions. By applying the concepts and skills introduced in this chapter, you will be able to explain what happens to the sugar in a candy bar you eat, what reaction occurs in a battery when you start your car, what may be causing the "ozone hole" over Antarctica, and how we might prevent the hole's growth.

Topic hierarchy

3.1a: Chemical Compounds
3.1b: Chemical Formulas
3.3: Composition of Chemical Compounds
3.4: Oxidation States
3.5: Importance of Nomenclature
3.6: Names and Formulas of Inorganic Compounds
3.7: Saturated Hydrocarbons

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3.1a: Chemical Compounds

Learning Objectives

- To understand the differences between covalent and ionic bonding.

The atoms in all substances that contain multiple atoms 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, the attractive interactions between atoms are called chemical bonds.

Chemical bonds are generally divided into two fundamentally different types: ionic and covalent. In reality, however, the bonds in most substances are neither purely ionic nor purely covalent, but lie on a spectrum between these extremes. Although purely ionic and purely covalent bonds represent extreme cases that are seldom encountered in any but very simple substances, a brief discussion of these two extremes helps explain why substances with 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, atoms are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share. This discussion of structures and formulas begins by describing covalent compounds. The energetic factors involved in bond formation are described in more quantitative detail in later.

Note

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 $3.1a.1$). Similarly, a few pure elements exist as polyatomic ("many atoms") molecules, such as elemental phosphorus and sulfur, which occur as P_4 and S_8 (part (b) in Figure $3.1a.1$).

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.

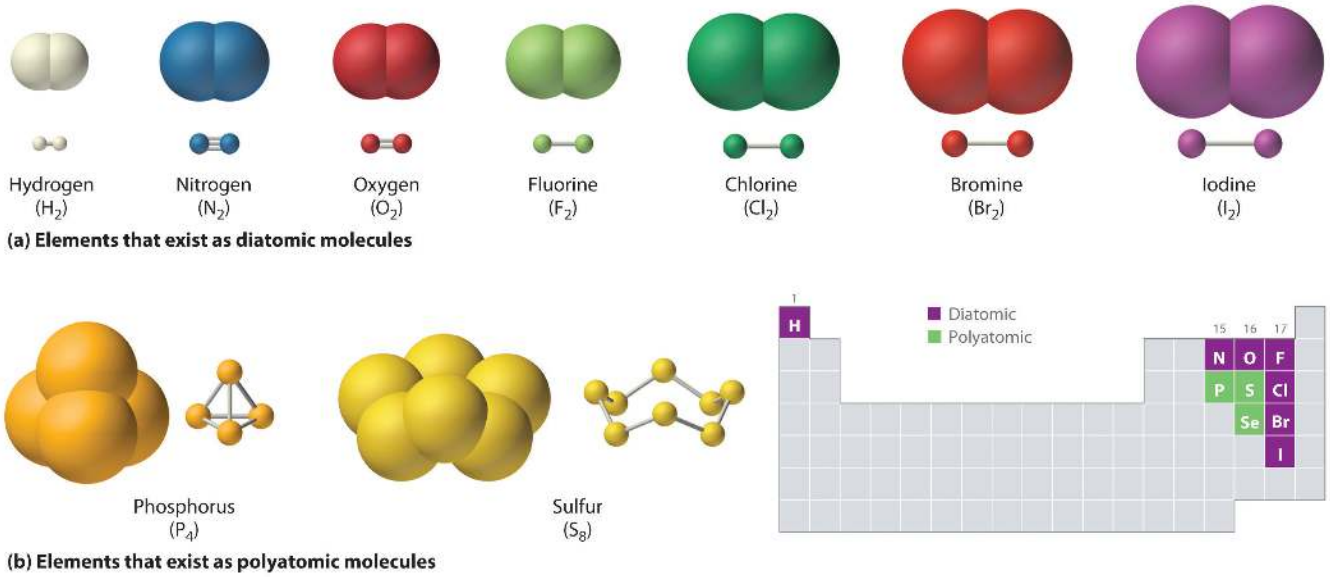


Figure 3.1a.1: Elements That Exist as Covalent Molecules. (a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula E2. (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as P4 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 predominantly contain 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, as 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, 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 elswhere.

Note

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 3.1a.1

Write the molecular formula of each compound.

a. 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.
b. Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
c. 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:

a.

- **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.

b.

- **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.

c.

- **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 3.1a.1

Write the molecular formula for each compound.

a. 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.
b. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.
c. 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:

a. N_2O
b. $C_{12}H_{22}O_{11}$
c. 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.

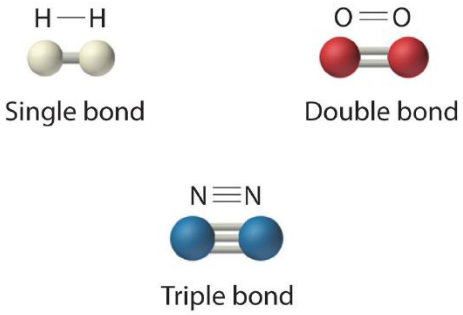


Figure 3.1*a*. 2: Molecules That Contain Single, Double, and Triple Bonds. Hydrogen (H_2) has a single bond between atoms. Oxygen (O_2) has a double bond between atoms, indicated by two lines (=). Nitrogen (N_2) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron pair.

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 (Figure 3.1*a*. 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. Hydrogen, oxygen, nitrogen, and carbon have very strong tendencies to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table 3.1*a*. 1).

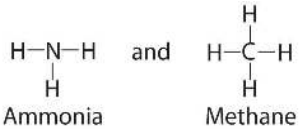
Table 3.1*a*. 1: The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

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 3.1*a*. 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 3.1*a*. 3, is tetrahedral: 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.

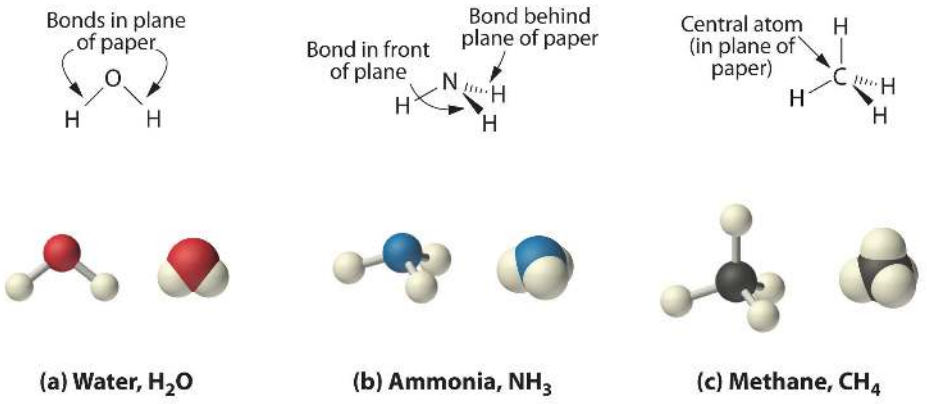


Figure 3.1a.3: The Three-Dimensional Structures of Water, Ammonia, and Methane. (a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.

Figures 3.1a.3-3.1a.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 used depends on which aspect of the structure should be emphasized and how much time and effort is required. Figure 3.1a.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 3.1a.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 3.1a.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 3.1a.4) and the perspective drawing (part (d) in Figure 3.1a.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 3.1a.4) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. In addition, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

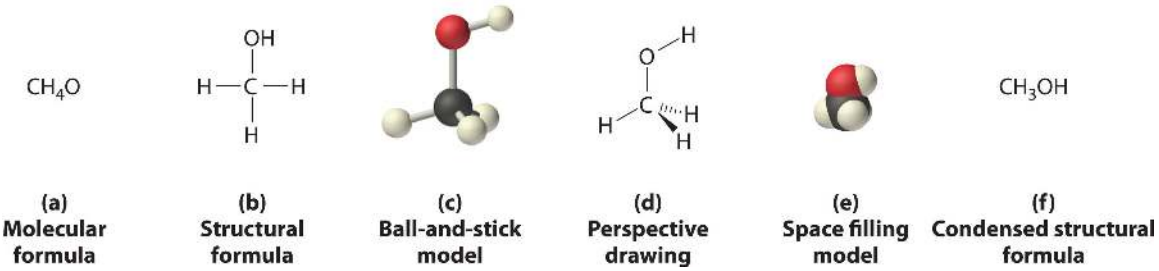


Figure 3.1a.4: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (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 3.1a.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 indicates 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-

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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 3.1a.2

Write the molecular formula for each compound. The condensed structural formula is given.

a. 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.
b. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
c. 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

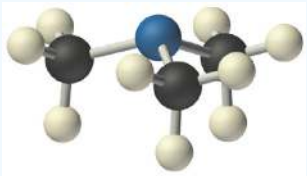
Strategy:

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.

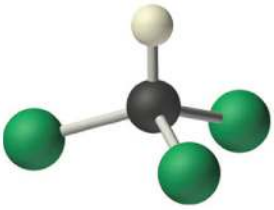
a. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
b. **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 $C_2H_6O_2$.
c. **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 3.1a.2

Write the molecular formula for each molecule.

a. 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 $CHCl_3$.
b. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is H_2NNH_2.
c. 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 a

$CHCl_3$

Answer b

N_2H_4

Answer c

$C_4H_{12}N_2$

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

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

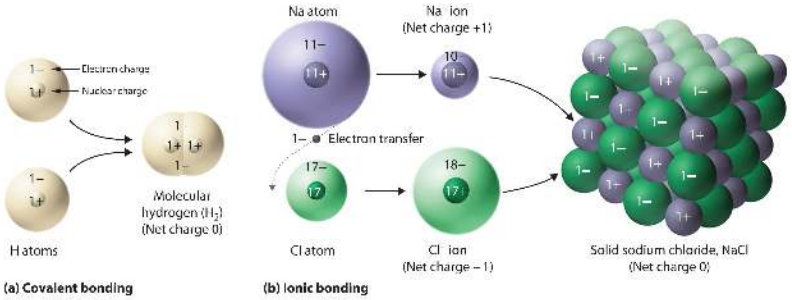


Figure $3.1a.5$: Covalent and Ionic Bonding. (a) In molecular hydrogen (H_2), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

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 $3.1a.5$). As shown in Equation 3.1.1, 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:

$$\text{electrostatic energy} \propto \frac{Q_1 Q_2}{r} \tag{3.1a.1}$$

where

- Q_1 and Q_2 are the electrical charges on particles 1 and 2, and

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- 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 $3.1a.6$, the strength of the interaction is proportional to the magnitude of the charges and decreases as the distance between the particles increases. These energetic factors are discussed in greater quantitative detail later.

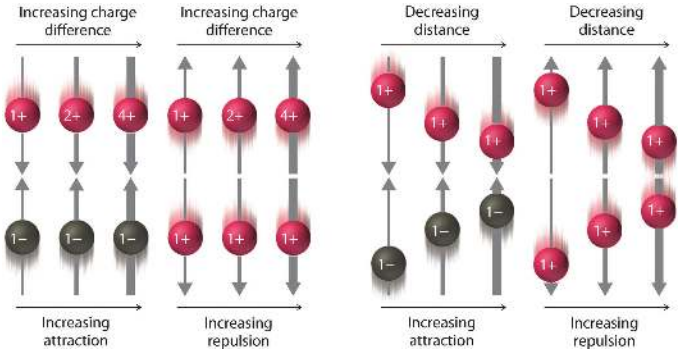


Figure $3.1a.6$: The Effect of Charge and Distance on the Strength of Electrostatic Interactions. As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (−…+) or repulsive (−…− or +…+) interactions. The strength of these interactions is represented by the thickness of the arrows.

Note

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

One example of an ionic compound is sodium chloride (NaCl), 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 $3.1a.5$. 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.

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. The charges of most monatomic ions derived from the main group elements can be predicted by simply looking at the periodic table and counting how many columns an element lies from the extreme left or right. For example, barium (in Group 2) forms Ba^{2+} to have the same number of electrons as its nearest noble gas, xenon; oxygen (in Group 16) forms O^{2-} to have the same number of electrons as neon; and cesium (in Group 1) forms Cs^+, which has the same number of electrons as xenon. Note that this method is ineffective for most of the transition metals, as discussed in Section 2.3. Some common monatomic ions are listed in Table $3.1a.2$.

Note

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 3.1a.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 3.1a.3

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

a. aluminum, used in the quantum logic clock, the world's most precise clock
b. selenium, used to make ruby-colored glass
c. 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:

a. **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.
b. **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.
c. **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 3.1a.3

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

a. calcium, used to prevent osteoporosis
b. iodine, required for the synthesis of thyroid hormones
c. zirconium, widely used in nuclear reactors

Answer:

a. Ca^{2+}
b. I^-
c. Zr^{4+}



Molecular and Ionic Compounds: https://youtu.be/zJejgCll1bw

Physical Properties of Ionic and Covalent Compounds

In general, ionic and covalent compounds have different physical properties. Ionic compounds form hard crystalline solids that melt at high temperatures and are resistant to evaporation. These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in part (a) in Figure $3.1a.8$ 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 $3.1a.8$ 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 low temperatures and evaporate 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 elsewhere. 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 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 $3.1a.3$.

Table $3.1a.3$: 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

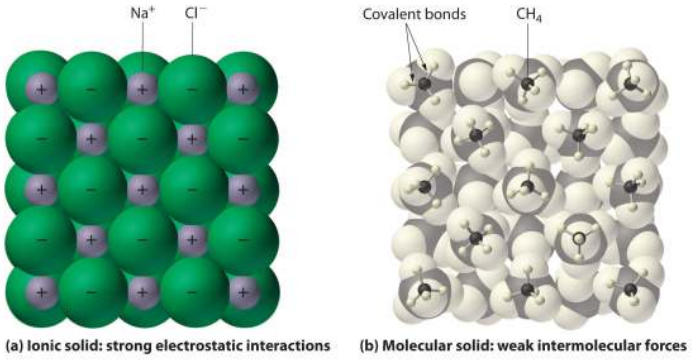


Figure 3.1*a*. 8: Interactions in Ionic and Covalent Solids. (a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane (CH4) molecules in solid methane, a 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.

- The Learning Objective of this Module is 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 has the empirical formula C_2H_5, but it contains two C_2H_5 formula units, giving a molecular formula of C_4H_{10}.

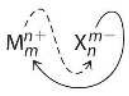
Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation 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

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

Binary Ionic Compounds

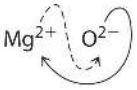
An ionic compound that contains only two elements, one present as a cation and one as an anion, is called a binary ionic compound. One example is $MgCl_2$, a coagulant used in the preparation of tofu from soybeans. For binary ionic compounds, the subscripts in the empirical formula can also be obtained 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, it is sometimes 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:

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

Example 3.1a.4

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

a. Ga^{3+} and As^{3-}
b. Eu^{3+} and O^{2-}
c. calcium and chlorine

Given: ions or elements

Asked for: empirical formula for binary ionic compound

Strategy:

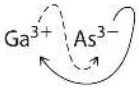
A If not given, determine the ionic charges based on the location of the elements in the periodic table.

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.

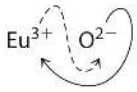
Solution

a. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga3As3:



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.

b. **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:

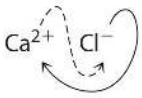


The subscript for Eu^{3+} is 2 (from O^{2-}), and the subscript for O^{2-} is 3 (from Eu^{3+}), giving Eu_2O_3; the subscripts cannot be reduced further. The empirical formula contains a positive charge of 2(+3) = +6 and a negative charge of 3(−2) = −6, for a net charge of 0. The compound Eu_2O_3 is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

c. **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:

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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 3.1a.4

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

a. Li^+ and N^{3-}
b. Al^{3+} and O^{2-}
c. lithium and oxygen

Answer:

a. Li_3N
b. Al_2O_3
c. Li_2O

Polyatomic Ions

Polyatomic ions are groups of atoms that bear net electrical charges, 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 3.1a.4.

Table 3.1a.4: 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

Formula	Name of Ion
ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate
MnO_4^-	permanganate
$CrO4_2^-$	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 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), 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 3.1a.5

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

a. Na^+ and HPO_4^{2-}
b. potassium cation and cyanide anion
c. 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 3.1a.4 "Common Polyatomic Ions and Their Names" 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:

a. **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.

b. **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.

c. **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 3.1*a*. 5

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

a. Ca^{2+} and $H_2PO_4^-$
b. sodium cation and bicarbonate anion
c. ammonium cation and sulfate anion

Answer:

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

Summary

- There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties.
- The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit.Contributors

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.

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.

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3.1b: Chemical Formulas

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3.3: Composition of Chemical Compounds

$$2 \times (1.0079\ amu) + 1 \times (15.9994\ amu) = 18.01528\ amu \tag{3.3.1}$$

If a substance exists as discrete molecules (as with atoms that are *chemically bonded* together) then the *chemical formula* **is** the *molecular formula*, and the *formula weight* **is** the *molecular weight*. For example, carbon, hydrogen and oxygen can chemically bond to form a molecule of the sugar **glucose** with the chemical and molecular formula of $C_6H_{12}O_6$. The formula weight and the molecular weight of glucose is thus:

$$6 \times (12\ amu) + 12 \times (1.00794\ amu) + 6 \times (15.9994\ amu) = 180.0\ amu \tag{3.3.2}$$

Ionic substances are not chemically bonded and do not exist as discrete molecules. However, they do associate in discrete ratios of ions. Thus, we can describe their formula weights, but not their *molecular weights*. Table salt (NaCl), for example, has a formula weight of:

$$23.0\ amu + 35.5\ amu = 58.5\ amu \tag{3.3.3}$$

Percentage Composition from Formulas

In some types of analyses of it is important to know the ***percentage by mass*** of each type of element in a compound. 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—is **constant** (although there are exceptions to this law). Take for example methane (CH_4) with a Formula and molecular weight:

$$1 \times (12.011\ amu) + 4 \times (1.008) = 16.043\ amu \tag{3.3.4}$$

the relative (mass) percentages of carbon and hydrogen are

$$\%C = \frac{1 \times (12.011\ amu)}{16.043 amu} = 0.749 = 74.9\% \tag{3.3.5}$$

$$\%H = \frac{4 \times (1.008\ amu)}{16.043\ amu} = 0.251 = 25.1\% \tag{3.3.6}$$

A more complex example is sucrose (table 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 the molecular formula of sucrose ($C_{12}H_{22}O_{11}$) is used to calculate the mass percentage of the component elements; the mass percentage can then 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. This information can be used to calculate the mass of each element in 1 mol of sucrose, which gives the molar mass of sucrose. These masses can then be used to calculate the percent composition of sucrose. To three decimal places, the calculations are the following:

$$\text{mass of C/mol of sucrose} = 12\ mol\ C \times \frac{12.011\ g\ C}{1\ mol\ C} = 144.132\ g\ C \tag{3.3.7}$$

$$\text{mass of H/mol of sucrose} = 22\ mol\ H \times \frac{1.008\ g\ H}{1\ mol\ H} = 22.176\ g\ C \tag{3.3.8}$$

$$\text{mass of O/mol of sucrose} = 11\ mol\ O \times \frac{15.999\ g\ O}{1\ mol\ O} = 175.989\ g\ O \tag{3.3.9}$$

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:

$$\text{mass \% C in Sucrose} = \frac{\text{mass of C/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{144.132\ g\ C}{342.297\ g/mol} \times 100 = 42.12\% \tag{3.3.10}$$

$$\text{mass \% H in Sucrose} = \frac{\text{mass of H/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{22.176\ g\ H}{342.297\ g/mol} \times 100 = 6.48\% \tag{3.3.11}$$

$$\text{mass \% O in Sucrose} = \frac{\text{mass of O/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{175.989\ g\ O}{342.297\ g/mol} \times 100 = 51.41\% \tag{3.3.12}$$

This can be checked by verifying that the sum of the percentages of all the elements in the compound is 100%:

$$42.12\% + 6.48\% + 51.41\% = 100.01\% \tag{3.3.13}$$

If the sum is not 100%, an error has been made in 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.

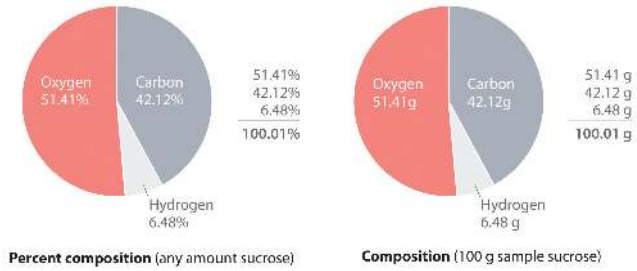
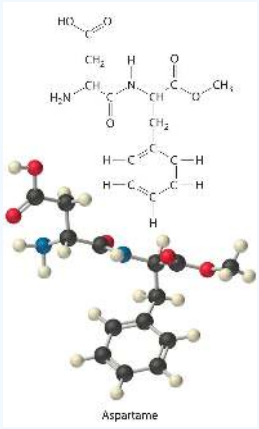


Figure 3.3.1: Percent and absolute composition of sucrose

It is also possible to calculate mass percentages using atomic masses and molecular masses, with atomic mass units. Because the answer 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 3.3.1

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



a. Calculate the mass percentage of each element in aspartame.
b. 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:

a.

A We calculate the mass of each element in 1 mol of aspartame and the molar mass of aspartame, here to three decimal places:

$$14\,C(14\,mol\,C)(12.011\,g/mol\,C) = 168.154\,g \tag{3.3.14}$$

$$18\,H(18\,mol\,H)(1.008\,g/mol\,H) = 18.114\,g \tag{3.3.15}$$

$$2\,N(2\,mol\,N)(14.007\,g/mol\,N) = 28.014\,g \tag{3.3.16}$$

$$+5\,O(5\,mol\,O)(15.999\,g/mol\,O) = 79.995\,g \tag{3.3.17}$$

$$C_{14}H_{18}N_2O_5 \text{molar mass of aspartame} = 294.277\,g/mol \tag{3.3.18}$$

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:

$$mass\%\,C = \frac{168.154\,g\,C}{294.277\,g\,aspartame} \times 100 = 57.14\%C \tag{3.3.19}$$

$$mass\%\,H = \frac{18.114\,g\,H}{294.277\,g\,aspartame} \times 100 = 6.16\%H \tag{3.3.20}$$

$$mass\%\,N = \frac{28.014\,g\,N}{294.277\,g\,aspartame} \times 100 = 9.52\% \tag{3.3.21}$$

$$mass\%\,O = \frac{79.995\,g\,O}{294.277\,g\,aspartame} \times 100 = 27.18\% \tag{3.3.22}$$

As a check, we can add the percentages together:

$$57.14\% + 6.16\% + 9.52\% + 27.18\% = 100.00\% \tag{3.3.23}$$

If you obtain a total that differs from 100% by more than about ±1%, there must be an error somewhere in the calculation.

b. **C** The mass of carbon in 1.00 g of aspartame is calculated as follows:

$$\text{mass of C} = 1.00\,g\,aspartame \times \frac{57.14\,g\,C}{100\,g\,aspartame} = 0.571\,g\,C \tag{3.3.24}$$

? Exercise 3.3.1: Aluminum Oxide

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



Percent Composition: https://youtu.be/HNS6lItns10

Determining the Empirical Formula of Penicillin

Just as the empirical formula of a substance can be used to determine its percent composition, the percent composition of a sample can be used 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 antibiotics are often taken 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 3.3.2), 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 3.3.2), Fleming called the active ingredient in the broth penicillin.

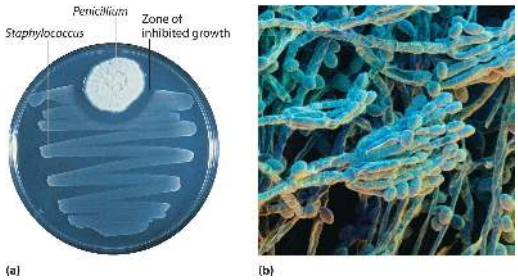


Figure 3.3.2 Penicillium. *(a) Penicillium mold is growing in a culture dish; the photo shows its effect on bacterial growth. (b) In this photomicrograph of Penicillium, its rod- and pencil-shaped branches are visible. The name comes from the Latin penicillus, meaning "paintbrush."*

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. Assuming 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, the mass percentages must be converted to relative numbers of atoms. For convenience, assume 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. Each mass is then divided by the molar mass of the element to determine how many moles of each element are present in the 100.0 g sample:

$$\frac{mass\,(g)}{molar\ mass\ (g/mol)} = (g)\left(\frac{mol}{g}\right) = mol \tag{3.3.25}$$

$$53.9\,g\,C\left(\frac{1\,mol\,C}{12.011\,g\,C}\right) = 4.49\,mol\,C \tag{3.3.26}$$

$$4.8\,g\,H\left(\frac{1\,mol\,H}{1.008g\,H}\right) = 4.8\,mol\,H \tag{3.3.27}$$

$$7.9\,g\,N\left(\frac{1\,mol\,N}{14.007\,g\,N}\right)=0.56\,mol\,N \tag{3.3.28}$$

$$9\,g\,S\left(\frac{1\,mol\,S}{32.065\,g\,S}\right)=0.28\,mol\,S \tag{3.3.29}$$

$$6.5\,g\,Na\left(\frac{1\,mol\,Na}{22.990\,g\,Na}\right)=0.28\,mol\,Na \tag{3.3.30}$$

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 give 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 needed for the empirical formula—the empirical formula expresses the relative numbers of atoms in the smallest whole numbers possible. To obtain whole numbers, 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 as follows:

$$C:\frac{4.49}{0.28}=16\quad H:\frac{4.8}{0.28}=17\quad N:\frac{0.56}{0.28}=2.0 \tag{3.3.31}$$

$$S:\frac{0.28}{0.28}=1.0\quad Na:\frac{0.28}{0.28}=1.0\quad O:\frac{1.12}{0.28}=4.0 \tag{3.3.32}$$

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 3.3.3) was not determined until 1948.

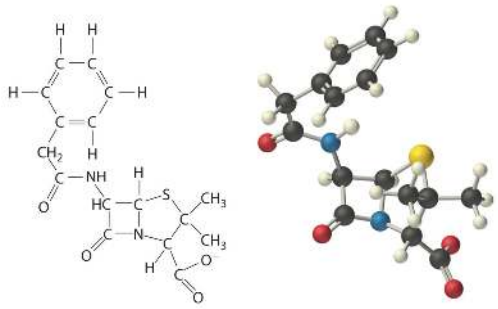


Figure 3.3.3 Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G

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, judgment must be exercised 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 one consider rounding to the nearest integer.

✔ Example 3.3.2: Calcium Phosphate in Toothpaste

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:

$$\text{moles Ca} = 38.77\,g\,Ca \times \frac{1\,mol\,Ca}{40.078\,g\,Ca} = 0.9674\,mol\,Ca \tag{3.3.33}$$

$$\text{moles P} = 19.97\,g\,P \times \frac{1\,mol\,P}{30.9738\,g\,P} = 0.6447\,mol\,Ca \tag{3.3.34}$$

$$\text{moles O} = 41.27\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 2.5800\,mol\,O \tag{3.3.35}$$

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:

$$P: \frac{0.6447\,mol\,P}{0.6447\,mol\,P} = 1.000 \quad Ca: \frac{0.9674}{0.6447} = 1.501 \quad O: \frac{2.5800}{0.6447} = 4.002 \tag{3.3.36}$$

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 Chapter 2 that phosphorus and oxygen form the phosphate ion (PO_4^{3-}; see Table 2.4). 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 3.3.2: Oklahoma City Bombing

Calculate the empirical formula of ammonium nitrate, an ionic compound that contains 35.00% nitrogen, 5.04% hydrogen, and 59.96% oxygen by mass. 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.



The Alfred P. Murrah Federal Building destroyed in the Oklahoma City bombing via chemical explosives (rapid chemical reactions that generate massive quantities of gases).

Answer

$N_2H_4O_3$ is $NH_4^+NO_3^-$, written as NH_4NO_3



Determining Empirical and Molecular Formulas from % Composition: https://youtu.be/E-MxBYw1TSI

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, chemists 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 3.3.3).

Consider glucose, the sugar that circulates in our blood to provide fuel for the body and brain. 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. Assuming 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, divide the mass of each element by its molar mass:

$$moles\,C = 39.68\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 3.304\,mol\,C \tag{3.3.37}$$

$$moles\,H = 6.58\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 6.53\,mol\,H \tag{3.3.38}$$

$$moles\,O = 53.79\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 3.362\,mol\,O \tag{3.3.39}$$

Once again, the subscripts of the elements in the empirical formula are found by dividing the number of moles of each element by the number of moles of the element present in the smallest amount:

$$C: \frac{3.304}{3.304} = 1.000 \quad H: \frac{6.53}{3.304} = 1.98 \quad O: \frac{3.362}{3.304} = 1.018 \tag{3.3.40}$$

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 the blood. At this point, it cannot be known whether glucose is CH_2O, $C_2H_4O_2$, or any other $(CH_2O)_n$. However, the experimentally determined molar mass of glucose (180 g/mol) can be used to resolve this dilemma.

First, 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,

$$\begin{aligned}\text{formula mass of} CH_2O &= \left[1\,mol C\left(\frac{12.011\,g}{1\,mol\,C}\right)\right] + \left[2\,mol\,H\left(\frac{1.0079\,g}{1\,mol\,H}\right)\right] + \left[1\,mole\,O\left(\frac{15.5994\,mol\,O}{1\,mol\,O}\right)\right] \\ &= 30.026g\end{aligned} \tag{3.3.41}$$

This is much smaller than the observed molar mass of 180 g/mol.

Second, determine the number of formula units per mole. For glucose, 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:

$$n = \frac{180\ g}{30.026\ g/CH_2O} = 5.99 \approx 6 CH_2O \text{ formula units} \tag{3.3.42}$$

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 3.3.4.

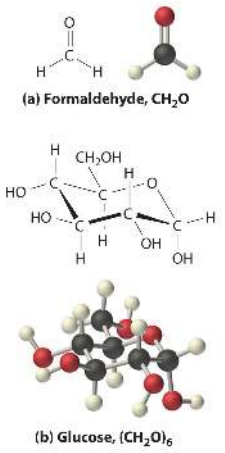


Figure 3.3.4 Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose

Example 3.3.3: Caffeine

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.

$$moles\ C = 49.18\ g\,C \times \frac{1\ mol\ C}{12.011\ g\,C} = 4.095\ mol\ C \tag{3.3.43}$$

$$moles\ H = 5.39\ g\,H \times \frac{1\ mol\ H}{1.0079\ g\,H} = 5.35\ mol\ H \tag{3.3.44}$$

$$moles\ N = 28.65\ g\,N \times \frac{1\ mol\ N}{14.0067\ g\,N} = 2.045\ mol\ N \tag{3.3.45}$$

$$moles\ O = 16.68\ g\,O \times \frac{1\ mol\ O}{15.9994\ g\,O} = 1.043\ mol\ O \tag{3.3.46}$$

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:

$$O: \frac{1.043}{1.043} = 1.000 \quad C: \frac{4.095}{1.043} = 3.926 \quad H: \frac{5.35}{1.043} = 5.13 \quad N: \frac{2.045}{1.043} = 1.960 \tag{3.3.47}$$

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:

$$4C \quad (4\,atoms\,C)(12.011\,g/atom\,C) = 48.044\,g \tag{3.3.48}$$

$$5H \quad (5\,atoms\,H)(1.0079\,g/atom\,H) = 5.0395\,g \tag{3.3.49}$$

$$2N \quad (2\,atoms\,N)(14.0067\,g/atom\,N) = 28.0134\,g \tag{3.3.50}$$

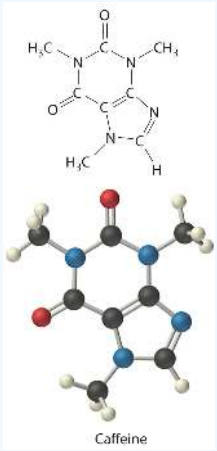
$$+1O \quad (1\,atom\,O)(15.9994\,g/atom\,O) = 15.9994\,g \tag{3.3.51}$$

$$C_4H_5N_2O \quad \text{formula mass of caffeine} = 97.096\,g \tag{3.3.52}$$

Dividing the measured molar mass of caffeine (196 g/mol) by the calculated formula mass gives

$$\frac{196 g/mol}{97.096 g/C_4H_5N_2O} = 2.02 \approx 2\,C_4H_5N_2O\,\text{empirical formula units} \tag{3.3.53}$$

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 3.3.3: Freon-114

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:

$$C_2Cl_2F_4 \tag{3.3.54}$$

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 3.3.5 and a typical combustion analysis is illustrated in Example 3.3.4.

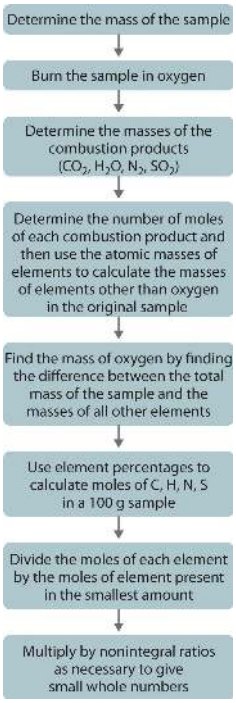


Figure 3.3.5: Steps for Obtaining an Empirical Formula from Combustion Analysis

Example 3.3.4

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:

$$mass\,of\,C = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,mol C}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C} \tag{3.3.55}$$

$$= 1.883 \times 10^{-2}\,g\,C \tag{3.3.56}$$

$$mass\,of\,H = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H} \tag{3.3.57}$$

$$= 1.264 \times 10^{-3}\,g\,H \tag{3.3.58}$$

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:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC \tag{3.3.59}$$

$$moles\,H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\,molH \tag{3.3.60}$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250 \tag{3.3.61}$$

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 3.3.4

a. 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.
b. 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:

a. The empirical formula is C_4H_5. (The molecular formula of xylene is actually C_8H_{10}.)
b. 33.81 mg of CO_2; 6.92 mg of H_2O

Summary

- 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.

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.

Contributors and Attributions

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3.4: Oxidation States

Learning Objectives

- To identify oxidation–reduction reactions in solution.

The term oxidation 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

Any oxidation must **ALWAYS** be accompanied by a reduction and vice versa.

Originally, the term reduction 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:

$$Cu_2O(s) + H_2(g) \rightarrow 2Cu(s) + H_2O(g) \tag{3.4.1}$$

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 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

$$4Al(s) + 3O_2 \rightarrow 2Al_2O_3(s) \tag{3.4.2}$$

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):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^{3+} + 6O^{2-} \tag{3.4.3}$$

Equation 3.4.1 and Equation 3.4.2 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 3.4.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$electrons\,lost = 4\ Al\ atoms \times \frac{3\ e^-\ lost}{Al\ atom} = 12\ e^-\ lost \tag{3.4.4}$$

electrons \, gained = 6 \, O \, atoms \times {2 \, e^- \, gained \over O \, atom} = 12 \, e^- \, gained \label{3.4.4a}

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained.

An additional example of a redox reaction, the reaction of sodium metal with oxygen in air, is illustrated in Figure 3.4.1.

Note

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. Previosuly, 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 3.4.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

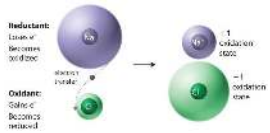


Figure 3.4.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

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.

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.

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 will discover in Chapter 6. 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.

The reduction of copper(I) oxide shown in Equation 3.4.5 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:

$$\overset{+1}{Cu}_2\overset{-2}{O}(s) + \overset{0}{H}_2(g) \rightarrow 2\overset{0}{Cu}(s) + \overset{+1}{H}_2\overset{-2}{O}(g) \tag{3.4.5}$$

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:

$$electrons\,lost = 2\,H\,atoms \times \frac{1\,e^-\,lost}{H\,atom} = 2\,e^-\,lost \tag{3.4.6}$$

$$electrons\,gained = 2\,Cu\,atoms \times \frac{1\,e^-\,gained}{Cu\,atom} = 2\,e^-\,gained \tag{3.4.7}$$

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 3.4.1

Assign oxidation states to all atoms in each compound.

a. sulfur hexafluoride (SF_6)
b. methanol (CH_3OH)
c. ammonium sulfate [$(NH_4)2SO_4$]
d. magnetite (Fe_3O_4)
e. 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:

a. 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

b. 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

c. 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 2.4). 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 SO42−, 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

d. 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:

$$[(4\text{ O atoms})(-2)]+[(3\text{ Fe atoms})\left(+\tfrac{8}{3}\right)]= 0$$

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."

e. 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

$$[(4\text{ H atoms})(+1)] + [(2\text{ O atoms})(-2)] = 0$$

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

$$[(2\text{ O atoms})(-2)] + [(1\text{ H atom})(+1)] = -3$$

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

$$\overset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\overset{-2}{O_2}\overset{+1}{H} \tag{3.4.8}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

? Exercise 3.4.1

Assign oxidation states to all atoms in each compound.

a. barium fluoride (BaF_2)
b. formaldehyde (CH_2O)
c. potassium dichromate ($K_2Cr_2O_7$)
d. cesium oxide (CsO_2)
e. ethanol (CH_3CH_2OH)

Answer:

a. Ba, +2; F, −1
b. C, 0; H, +1; O, −2
c. K, +1; Cr, +6; O, −2
d. Cs, +1; O, −½
e. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

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 3.4.1). 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) \label{3.4.5}

In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.



Figure 3.4.2: 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

Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \label{3.4.5}

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:

Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \label{3.4.5}

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 3.4.8) and the reduction of silver salts by copper (Equation 3.4.9 and Figure 3.4.2):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s) \tag{3.4.9}$$

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \tag{3.4.10}$$

The reaction in Equation 3.4.8 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 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, 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:

$$Zn(s) + Mg^{2+}(aq) \not\rightarrow Zn^{2+}(aq) + Mg(s) \tag{3.4.11}$$

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s) \tag{3.4.12}$$

Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure 3.4.4), 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, which have the greatest tendency to be oxidized. (located at the top of the series) and which are inert metals, which have the least tendency to be oxidized. (at the bottom of the series).

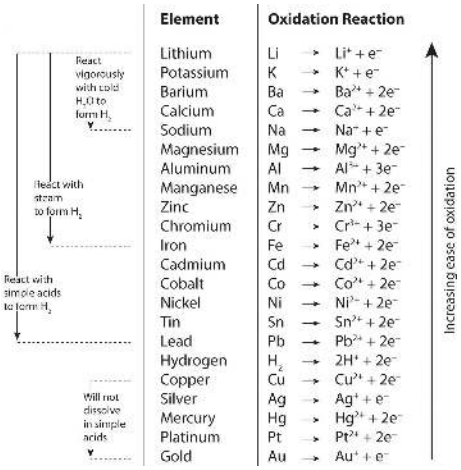


Figure 3.4.4: The Activity Series

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 3.4.4, 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 3.4.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

✔ Example 3.4.2

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 .3.4.4 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:

$$Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s) \tag{3.4.13}$$

   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:

$$Pb(s) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + H_2(g) \tag{3.4.14}$$

   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 3.4.2

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

- Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation.

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 3.4.1), 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 3.4.3), 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.

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3.5: Importance of Nomenclature

The primary function of chemical nomenclature is to ensure that a spoken or written chemical name leaves no ambiguity concerning which chemical compound the name refers to: each chemical name should refer to a single substance. A less important aim is to ensure that each substance has a single name (although a limited number of alternative names is acceptable in some cases). The form of nomenclature used depends on the audience to which it is addressed. As such, no single ***correct*** form exists, but rather there are different forms that are more or less appropriate in different circumstances. A common name will often suffice to identify a chemical compound in a particular set of circumstances. However, in a few specific circumstances (such as the construction of large indices), it becomes necessary to ensure that each compound has a unique name.

In discussing chemistry nomenclatures is it necessary to identify the type of compound including stoichiometry and type of constituent atoms. The first separation of importance is to distinguish between **inorganic** and **organic** compounds. Unfortunately, this separation is not always clear. even to experienced chemists. Historically (two centuries ago) the definitions were that inorganic compounds were synthesized by geological systems and organic compounds were found in biological systems. The modern definitions argues that organic compounds are any molecule containing carbon and by default this means that inorganic chemistry deals with molecules lacking carbon. The confusion arise when chemists that study carbon based materials like diamond or graphite, but that argument is beyond the scope of this text. The following sections presents the current nomenclature rules for inorganic and organic molecules.

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3.6: Names and Formulas of Inorganic Compounds

Learning Objectives

- To name ionic compounds.

The empirical and molecular formulas discussed in the preceding section are precise and 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, many compounds have the same empirical and molecular formulas but different arrangements of atoms, which differences 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 several), 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, a systematic nomenclature is used 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, familiarity with the common name as well as the systematic one is required. The objective of this and the next two sections is to teach how to write the formula for a simple inorganic compound from its name—and vice versa—and introduce some frequently-encountered common names.

Binary ionic compounds contain only two elements. The procedure for naming such compounds is outlined in Figure 3.6.1 and uses the following steps:

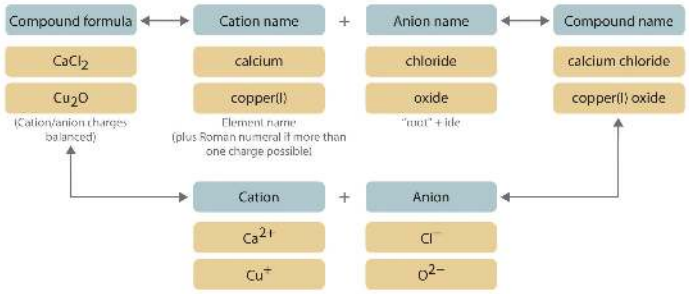


Figure 3.6.1: Naming an Ionic Compound

1. Place the ions in their proper order: cation and then anion.

2. Name the cation.

    a. **Metals that form only one cation**. As noted previosuly, 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.

    b. **Metals that form more than one cation**. As shown in Figure 3.6.2, 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, it is important to recognize these common names because they are still often used. For example, on the label of dental 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 listed in Table 3.6.1, 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 3.6.1: Common Cations of Metals That Form More Than One Ion

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

* Not widely used.

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

c. **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.

a. **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 Table 2.2

b. **Polyatomic anions**. Polyatomic anions typically have common names that must be memorized; 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 3.6.3 "The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present." 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.

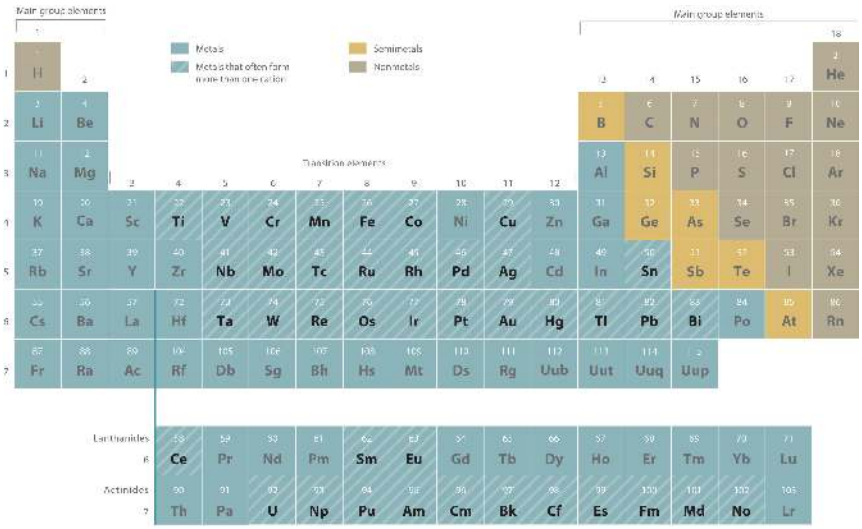


Figure 3.6.2: Metals That Form More Than One Cation and Their Locations in the Periodic Table

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. The charge of the ions must be considered 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, arithmetic indicates 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 3.6.1, Table 2.2, Table 2.4, and Table 3.6.1 as needed.

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

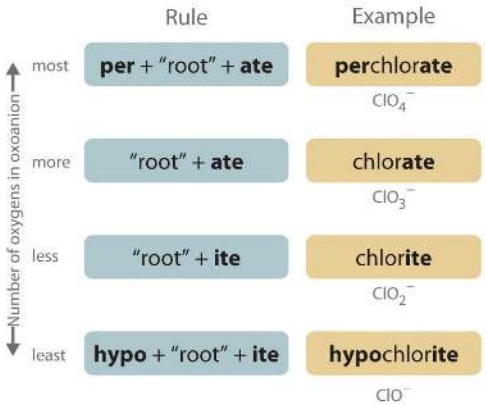


Figure 3.6.3: The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present

Note

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 3.6.1

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

a. LiCl
b. $MgSO_4$
c. $(NH_4)_3PO_4$
d. 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 3.6.1), 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:

a. **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.

b. **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.

c. **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.

d. **A B** The cation is a transition metal that often forms more than one cation (Table 3.6.1). 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.



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

? Exercise 3.6.1

Exercise

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

a. $CuCl_2$
b. $MgCO_3$
c. $FePO_4$

Answer:

a. copper(II) chloride (or cupric chloride)
b. magnesium carbonate

c. iron(III) phosphate (or ferric phosphate)

Example 3.6.2

Write the formula for each compound.

a. calcium dihydrogen phosphate
b. aluminum sulfate
c. 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 and 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:

a. **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.

b. **A** Aluminum, near the top of group 13 in the periodic table, forms only one cation, Al^{3+} (Figure 3.6.2 "Metals That Form More Than One Cation and Their Locations in the Periodic Table"). 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.

c. **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 3.6.2

Write the formula for each compound.

a. barium chloride
b. sodium carbonate
c. iron(III) hydroxide

Answer:

a. $BaCl_2$
b. Na_2CO_3
c. $Fe(OH)_3$

Summary

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

Ionic compounds are named according to systematic procedures, although common names are widely used. Systematic nomenclature enables chemists 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.

Learning Objectives

- To describe the composition of a chemical compound.
- To name covalent compounds that contain up to three elements.

As with ionic compounds, the system for naming covalent compounds enables chemists to write the molecular formula from the name and vice versa. This and the following section describe the rules for naming simple covalent compounds, beginning with inorganic compounds and then turning to simple organic compounds that contain only carbon and hydrogen.

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 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

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



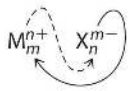
Nomenclature of Metals: https://youtu.be/zVhGxYTgRk0



Nomenclature of Transition Metals: https://youtu.be/gIaRpko0A_A

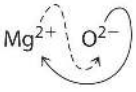
Binary Ionic Compounds

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, it is sometimes 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 3.6.1

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

a. Ga^{3+} and As^{3-}
b. Eu^{3+} and O^{2-}
c. calcium and chlorine

Given: ions or elements

Asked for: empirical formula for binary ionic compound

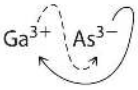
Strategy:

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.

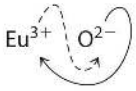
Solution

a. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga3As3:



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.

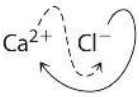
b. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



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.

c. **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 3.6.1

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

a. Li^+ and N^{3-}
b. Al^{3+} and O^{2-}
c. lithium and oxygen

Answer:

a. Li_3N
b. Al_2O_3
c. Li_2O

Polyatomic Ions

Polyatomic ions are groups of atoms that bear net electrical charges, 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 3.6.1.

Table 3.6.1: Common Polyatomic Ions and Their Names

Formula	Name of Ion	Formula	Name of Ion
NH_4^+	ammonium	HPO_4^{2-}	hydrogen phosphate
$CH_3NH_3^+$	methylammonium	$H_2PO_4^-$	dihydrogen phosphate
OH^-	hydroxide	ClO^-	hypochlorite
O_2^{2-}	peroxide	ClO_2^-	chlorite
CN^-	cyanide	ClO_3^-	chlorate
SCN^-	thiocyanate	ClO_4^-	perchlorate
NO_2^-	nitrite	MnO_4^-	permanganate
NO_3^-	nitrate	$CrO4_2^-$	chromate
CO_3^{2-}	carbonate	$Cr_2O_7^{2-}$	dichromate
HCO_3^-	hydrogen carbonate, or bicarbonate	$C_2O_4^{2-}$	oxalate
SO_3^{2-}	sulfite	HCO_2^-	formate
SO_4^{2-}	sulfate	$CH_3CO_2^-$	acetate
HSO_4^-	hydrogen sulfate, or bisulfate	$C_6H_5CO_2^-$	benzoate
PO_4^{3-}	phosphate		

The method 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), 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 3.6.2

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

a. Na^+ and HPO_4^{2-}
b. potassium cation and cyanide anion
c. 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 3.6.1 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:

a. **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.
b. **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.
c. **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 3.6.2

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

a. Ca^{2+} and $H_2PO_4^-$
b. sodium cation and bicarbonate anion
c. ammonium cation and sulfate anion

Answer:

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



Polyatomics: https://youtu.be/kTSPkzDcntA

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 3.6.1: Loss of Water from a Hydrate with Heating. (left) 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 "anhydrous" $CuSO_4$ (right). Images used with permission from Wikipedia.

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $CaSO_4{\cdot}½H2O$ 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.

Binary Inorganic Compounds

Binary covalent compounds—covalent compounds that contain only two elements—are named using a procedure similar to that used for simple ionic compounds, but prefixes are added as needed to indicate the number of atoms of each kind. The procedure, diagrammed in Figure 3.6.2 consists of the following steps:

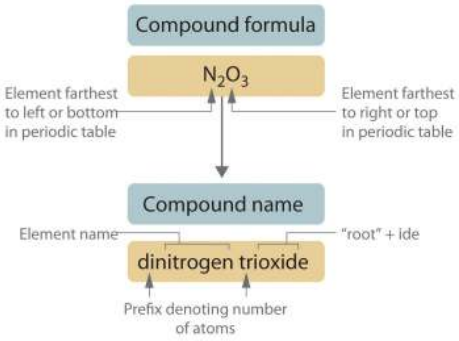


Figure 3.6.2 Naming a Covalent Inorganic Compound

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 3.6.2). The prefix *mono-* ("one") is used only when absolutely necessary to avoid confusion, just as the subscript 1 is omitted when writing molecular formulas.

        To demonstrate steps 1 and 2a, HCl is named hydrogen chloride (because hydrogen is to the left of chlorine in the periodic table), and PCl_5 is 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 3.6.2: 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 2.13.
    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.
2. Certain compounds are *always* called by the common names that were assigned before 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, requiring familiarity with both. 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

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 3.6.3

Write the name of each binary covalent compound.

a. SF_6
b. N_2O_4
c. 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 3.6.2 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:

a. **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 3.6.2). The compound is sulfur hexafluoride.
b. **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 3.6.2 "Prefixes for Indicating the Number of Atoms in Chemical Names", 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.
c. **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.

Example 3.6.3

Write the name of each binary covalent compound.

a. IF_7
b. N_2O_5
c. OF_2

Answer

a. iodine heptafluoride
b. dinitrogen pentoxide
c. oxygen difluoride

Example 3.6.4

Write the formula for each binary covalent compound.

a. sulfur trioxide
b. diiodine pentoxide

Given: name of compound

Asked for: formula

Strategy:

List the elements in the same order as in the formula, use Table 3.6.2 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:

a. 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.
b. 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 3.6.4

Write the formula for each binary covalent compound.

a. silicon tetrachloride
b. disulfur decafluoride

Answer

a. $SiCl_4$
b. S_2F_{10}

The structures of some of the compounds in Examples 3.6.3 and 3.6.4 are shown in Figure 3.6.2 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 mastering the material discussed later on this course, one is able to predict the compositions and structures of compounds of this type with a high degree of accuracy.

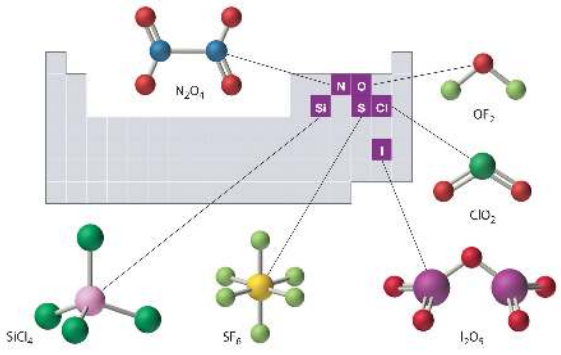


Figure 3.6.2 The Structures of Some Covalent Inorganic Compounds and the Locations of the "Central Atoms" in the Periodic Table. The compositions and structures of covalent inorganic compounds are not random and can be predicted from the locations of the component atoms in the periodic table.

https://chem.libretexts.org/@go/page/36983



Nomenclature of Nonmetals: https://youtu.be/VgHCrtpDWJk

The Learning Objective of this Module is 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 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 later, 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 3.6.3). 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

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

Table 3.6.3: 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: sulfate becomes sulfuric and phosphate becomes phosphoric.
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.

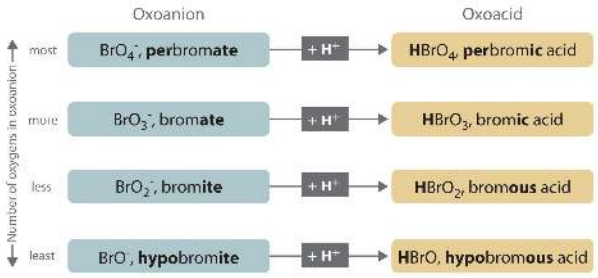


Figure 3.6.3: The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions

The relationship between the names of the oxoacids and the parent oxoanions is illustrated in Figure 3.6.3, and some common oxoacids are in Table 3.6.4.

Table 3.6.4: 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 3.6.5

Name and give the formula for each acid.

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

Given: anion

Asked for: parent acid

Strategy:

Refer to Table 3.6.3 and Table 3.6.4 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 3.6.3 or Table 3.6.4, so we must use the information given previously to derive the name of the acid from the name of the polyatomic anion.

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

? Exercise 3.6.5

Name and give the formula for each acid.

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

Answer:

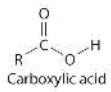
a. perbromic acid; $HBrO_4$
b. arsenous acid; H_3AsO_3



Nomenclature of Acids: https://youtu.be/in46UUzmSO4

Organic Acids

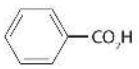
Many organic compounds contain the carbonyl group, in which there is a carbon–oxygen double bond. In carboxylic acids, an –OH group is covalently bonded to the carbon atom of the carbonyl group. Their general formula is RCO_2H, sometimes written as RCOOH:



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 Table 3.6.5.

***Table* 3.6.5**: *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

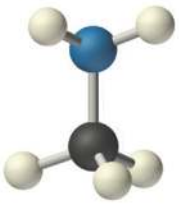
Although carboxylic acids are covalent compounds, when they dissolve in water, they dissociate to produce H^+ ions (just like any other acid) and RCO_2^- ions. Note that only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an H^+ ion. In contrast, the hydrogen atom attached 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

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 NH3 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

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.

Summary

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

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. 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.

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3.7: Saturated Hydrocarbons

Approximately one-third of the compounds produced industrially are organic compounds. All living organisms are composed of organic compounds, as are most foods, medicines, clothing fibers, and plastics. 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 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 following: 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 3.7.1, and the names and condensed structural formulas for the first 10 straight-chain alkanes are in Table 3.7.1. The names of all alkanes end in *-ane*, and their boiling points increase as the number of carbon atoms increases.

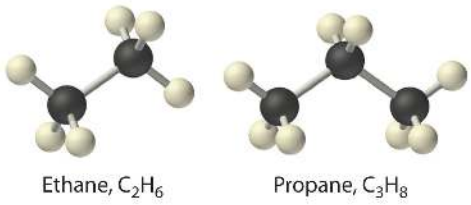
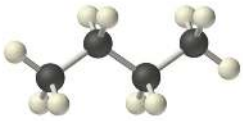


Figure 3.7.1: Straight-Chain Alkanes with Two and Three Carbon Atoms

Table 3.7.1: The 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:

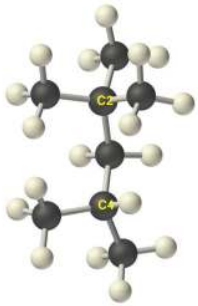


n-Butane, C_4H_{10}



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, Section 2.6 states that one of the major components of gasoline is commonly called isooctane; its structure is as follows:



Isooctane (2,2,4-trimethylpentane)

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 3.7.2). The names of alkenes that have more than three carbon atoms use the same stems as the names of the alkanes (Table 3.7.1 "The First 10 Straight-Chain Alkanes") but end in *-ene* instead of *-ane*.

As with alkanes, 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 3.7.2). 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.

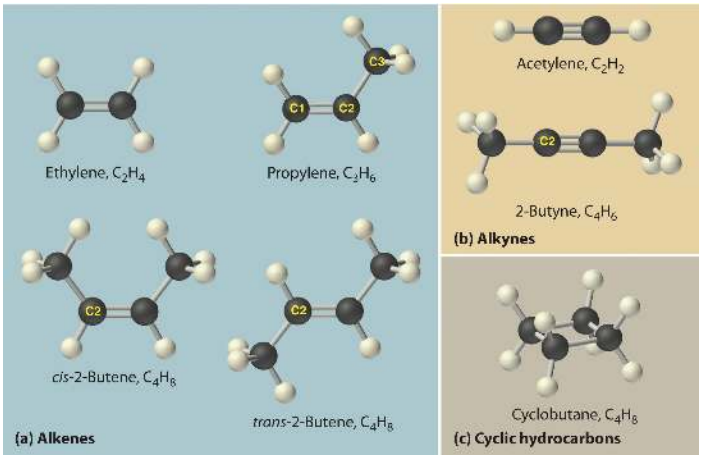
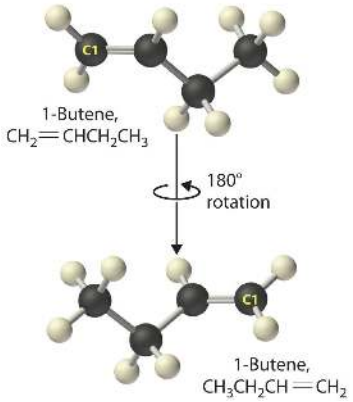


Figure 3.7.2: Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons. The positions of the carbon atoms in the chain are indicated by C_1 or C_2.

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. It is important to be able to recognize the same structure no matter what its orientation.*

Note

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 3.7.2). 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 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

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SECTION OVERVIEW

Unit II: Chemical Reactions

4: Chemical Reactions

4.1: Chemical Reactions and Chemical Equations
4.2: Chemical Equations and Stoichiometry
4.3: Solution Concentrations
4.4: Determining the Limiting Reactant
4.5: Other Practical Matters in Reactions

5: Reactions in Aqueous Solutions

5.1: The Nature of Aqueous Solutions
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CHAPTER OVERVIEW

4: Chemical Reactions



UC Davis CHE 2A: General Chemistry

Instructor: Gulacar

Chem 2A *Chem 2B* *Chem 2C*

Reading Assignments
Exercises
Worksheets
Homework

Unit I: Atomic Theory **Unit II: Chemical Reactions** **Unit III: Gases** **Unit IV: Electronic Structure and Bonding**

Template:HideTOC

We begin this chapter by describing the relationship between the mass of a sample of a substance and its composition. We then develop methods for determining the quantities of compounds produced or consumed in chemical reactions, and we describe some fundamental types of chemical reactions. By applying the concepts and skills introduced in this chapter, you will be able to explain what happens to the sugar in a candy bar you eat, what reaction occurs in a battery when you start your car, what may be causing the “ozone hole” over Antarctica, and how we might prevent the hole’s growth.

4.1: Chemical Reactions and Chemical Equations
4.2: Chemical Equations and Stoichiometry
4.3: Solution Concentrations
4.4: Determining the Limiting Reactant
4.5: Other Practical Matters in Reactions

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4.1: Chemical Reactions and Chemical Equations

$$2H_2 + O_2 \rightarrow 2H_2O \tag{4.1.1}$$

Chemical formulas and other symbols are used to indicate the starting materials, or reactants, which by convention are written on the left side of the equation, and the final compounds, or products, which are written on the right. An arrow points from the reactant to the products. The chemical reaction for the ammonium dichromate volcano in Figure 4.1.1 is

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O \tag{4.1.2}$$

$$reactant \qquad products \tag{4.1.3}$$

The arrow is read as “yields” or “reacts to form.” Equation 4.1.1 indicates 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 follows:

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_{3\ (s)} + N_{2\ (g)} + 4H_2O_{(g)} \tag{4.1.4}$$

Equation 4.1.2 is identical to Equation 4.1.1 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 Equations 4.1.1 and 4.1.2. Each side of the reaction 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. Equations 4.1.1 and 4.1.2 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.

of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.



Introduction to Chemical Reaction Equations: https://youtu.be/5mjawuf7K2Q

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4.2: Chemical Equations and Stoichiometry

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{4.2.1}$$

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 does not 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 is to write the balanced chemical equation for the reaction. Inspection shows that it is balanced as written, so the strategy outlined in , can be adapted 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:

$$moles\ glucose = 45.3\ g\ glucose \times \frac{1\ mol\ glucose}{180.2\ g\ glucose} = 0.251\ mol\ glucose \tag{4.2.2}$$

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. The number of moles of CO_2 produced is thus

$$moles\ CO_2 = mol\ glucose \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \tag{4.2.3}$$

$$= 0.251\ mol\ glucose \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \tag{4.2.4}$$

$$= 1.51\ mol\ CO_2 \tag{4.2.5}$$

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:

$$mass\ of\ CO_2 = 1.51\ mol\ CO_2 \times \frac{44.010\ g\ CO_2}{1\ mol\ CO_2} = 66.5\ g\ CO_2 \tag{4.2.6}$$

$$45.3\ g\ glucose \times \frac{1\ mol\ glucose}{180.2\ g\ glucose} \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \times \frac{44.010\ g\ CO_2}{1\ mol\ CO_2} = 66.4\ g\ CO_2 \tag{4.2.7}$$

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 , .) This amount of gaseous carbon dioxide occupies an enormous volume—more than 33 L. Similar methods can be used to calculate the amount of oxygen consumed or the amount of water produced.

The balanced chemical equation was used to calculate the mass of product that is formed from a certain amount of reactant. It can also be used 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.

✔ 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.



Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): https://youtu.be/74mHV0CZcjw

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4.3: Solution Concentrations

Learning Objectives

- To describe the concentrations of solutions quantitatively

Many people 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 of a solution is 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 solution reactions. Chemists use many different methods 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 defined as the number of moles of solute present in exactly 1 L of solution. It is, equivalently, 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 molar concentration of a solute. Therefore,

$$[\text{sucrose}] = 1.00\ \text{M} \tag{4.3.1}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.3.2}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{4.3.3}$$

Figure 4.3.1 illustrates the use of Equation 4.3.2 and Equation 4.3.3.

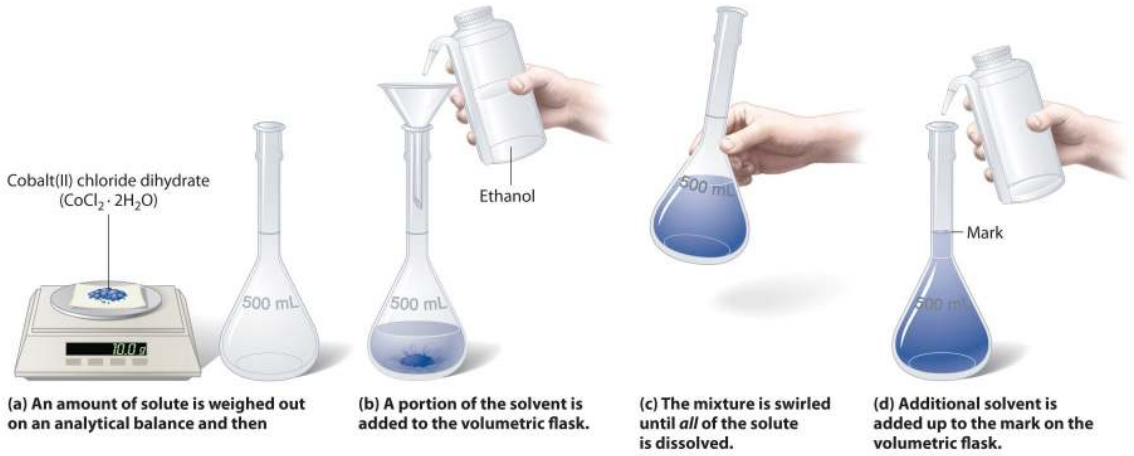


Figure 4.3.1: Preparation of a Solution of Known Concentration Using a Solid Solute

Example 4.3.1

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 4.3.2 or Equation 4.3.3, 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 4.3.2 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 4.3.1

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 (Table 4.3.1).

Table 4.3.1: 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



Calculations Involving Molarity (M): https://youtu.be/TVTCvKoSR-Q

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 4.3.1 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 4.3.2, for some substances this effect can be significant, especially for concentrated solutions.

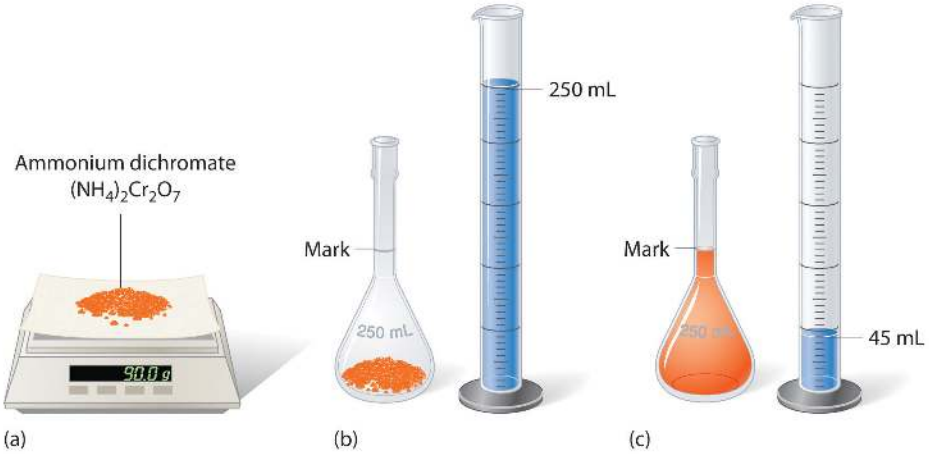


Figure 4.3.2: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

Example 4.3.2

The solution in Figure 4.3.1 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 4.3.2

The solution shown in Figure 4.3.2 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 4.3.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 4.3.3.

✓ Example 4.3.3

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:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{mol/L} = moles$$

$$500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.155\ mol\ glucose$$

B We then convert the number of moles of glucose to the required mass of glucose:

$$mass\ of\ glucose = 0.155\ \cancel{mol\ glucose}\left(\frac{180.16\ g\ glucose}{1\ \cancel{mol\ glucose}}\right) = 27.9\ g\ glucose$$

? Exercise 4.3.3

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 4.3.3. 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 5.5.4 demonstrates the calculations involved in diluting a concentrated stock solution.



Figure 4.3.3: 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 4.3.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4.3.3?

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 4.3.3 was 0.310 M glucose. We begin by using Equation 4.3.4 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 4.3.4 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 4.3.4

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

Calculating Moles from Volume

Quantitative calculations involving reactions in solution are carried out with *masses*, however, *volumes* of solutions of known concentration are used to determine the number of moles of reactants. Whether dealing with volumes of solutions of reactants or masses of reactants, the coefficients in the balanced chemical equation give the number of moles of each reactant needed and the number of moles of each product that can be produced.

The flowchart for stoichiometric calculations illustrated in Figure 4.3.4 shows that in 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 can be used to determine the amounts of other species.

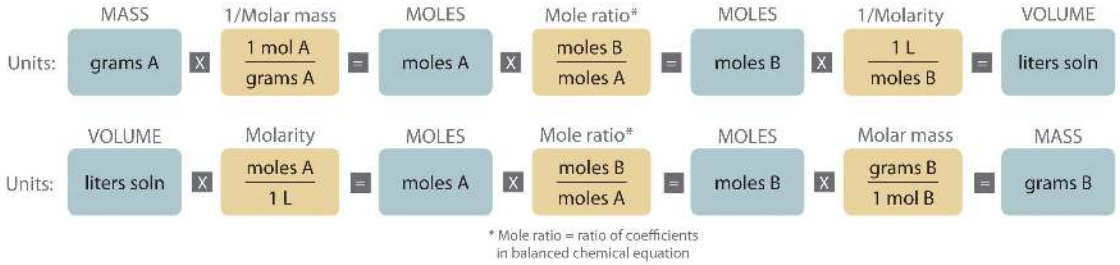


Figure 4.3.4: An Expanded Flowchart for Stoichiometric Calculations. Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

Note

The 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 4.3.5: Extraction of Gold

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:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s) \tag{4.3.4}$$

What mass of gold can be recovered from 400.0 L of a 3.30×10^{-4} M solution of $[Au(CN)_2]^-$?

Given: chemical equation and molarity and volume of reactant

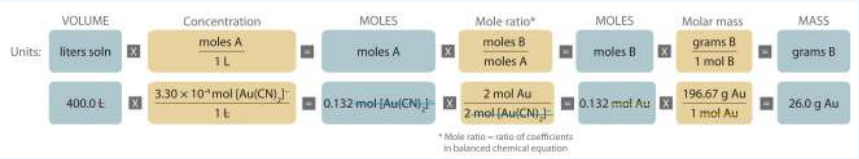
Asked for: mass of product

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:

A The equation is balanced as written; proceed to the stoichiometric calculation. Figure 4.3.2 is adapted for this particular problem as follows:



As indicated in the strategy, 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:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \tag{4.3.5}$$

$$= 400.0\ \cancel{L}\left(\frac{3.30 \times 10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \tag{4.3.6}$$

B Because the coefficients of gold and the $[Au(CN)_2]^-$ ion are the same in the balanced chemical equation, assuming that Zn(s) is present in excess, the number of moles of gold produced is the same as the number of moles of $[Au(CN)_2]^-$ (i.e., 0.132 mol of Au). The problem asks for the mass of gold that can be obtained, so the number of moles of gold must be converted to the corresponding mass using the molar mass of gold:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \tag{4.3.7}$$

$$= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \tag{4.3.8}$$

At a 2011 market price of over $1400 per troy ounce (31.10 g), this amount of gold is worth $1170.

$$26.0\ \cancel{g\ Au} \times \frac{1\ \cancel{troy\ oz}}{31.10\ \cancel{g}} \times \frac{\$1400}{1\ \cancel{troy\ oz\ Au}} = \$1170$$

? Exercise 4.3.5: Lanthanum Oxalate

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

Ion Concentrations in Solution

In Example 4.3.2, the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL were calculated to be 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:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{4.3.9}$$

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 4.3.4).

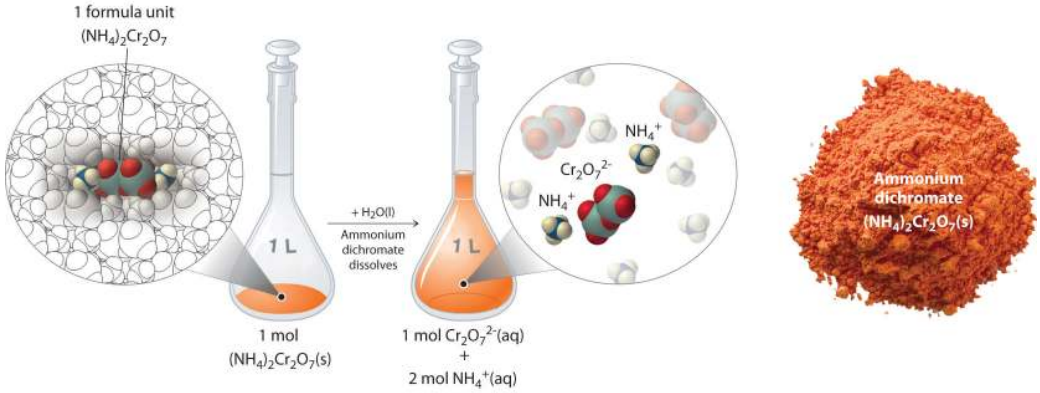


Figure 4.3.4: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

When carrying out a chemical reaction using a solution of a salt such as ammonium dichromate, it is important 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 4.3.6

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 4.1 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:

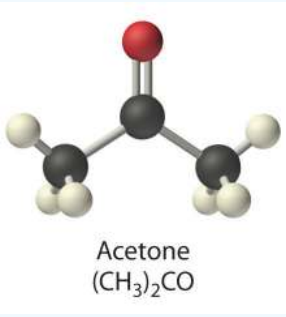
$$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

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 4.3.6

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.0012 M $Ba(OH)_2$
b. 0.17 M Na_2SO_4
c. 0.50 M $(CH_3)_2CO$, commonly known as acetone



Answer

a. $[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$
b. $[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$
c. $[(CH_3)_2CO] = 0.50\ M$



Concentration of Ions in Solution from a Soluble Salt: https://youtu.be/qsekSJBLemc

Summary

- Solution concentrations are typically expressed as molarities and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.
- **definition of molarity:**

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{4.3.10}$$

- **relationship among volume, molarity, and moles**:

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{4.3.11}$$

- **relationship between volume and concentration of stock and dilute solutions**:

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{4.3.12}$$

The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed in terms of **molarity**, defined as 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.

Contributors and Attributions

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4.4: Determining the Limiting Reactant

Learning Objectives

- To understand the concept of limiting reactants and quantify incomplete reactions

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.

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

$$1\text{ box mix} + 2\text{ eggs} \rightarrow 1\text{ batch brownies} \tag{4.4.1}$$

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 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. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

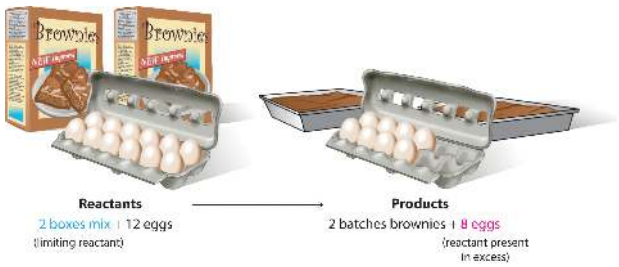


Figure 4.4.1: The Concept of a Limiting Reactant in the Preparation of Brownies

Now consider 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:

$$TiCl_4(g) + 2\,Mg(l) \rightarrow Ti(s) + 2\,MgCl_2(l) \tag{4.4.2}$$

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, magnesium metal is the limiting reactant in the production of metallic titanium.



Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)

With 1.00 kg of titanium tetrachloride and 200 g of magnesium metal, how much titanium metal can be produced according to the equation above? 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, 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:

$$moles\,TiCl_4 = \frac{mass\,TiCl_4}{molar\,mass\,TiCl_4} \tag{4.4.3}$$

$$= 1000\,g\,TiCl_4 \times \frac{1\,mol\,TiCl_4}{189.679\,g\,TiCl_4} = 5.272\,mol\,TiCl_4 \tag{4.4.4}$$

$$moles\,Mg = \frac{mass\,Mg}{molar\,mass\,Mg} \tag{4.4.5}$$

$$= 200\,g\,Mg \times \frac{1\,mol\,Mg}{24.305\,g\,Mg} = 8.23\,mol\,Mg \tag{4.4.6}$$

2. There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol\,Mg}{mol\,TiCl_4} = \frac{8.23\,mol}{5.272\,mol} = 1.56 \tag{4.4.7}$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2\,mol\,Mg}{1\,mol\,TiCl_4} = 2 \tag{4.4.8}$$

there is not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, there are 8.23 mol of Mg, so (8.23 ÷ 2) = 4.12 mol of $TiCl_4$ are required for complete reaction. Because there are 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 there are only 8.23 mol. Therefore, 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:

$$moles\,Ti = 8.23\,mol\,Mg = \frac{1\,mol\,Ti}{2\,mol\,Mg} = 4.12\,mol\,Ti \tag{4.4.9}$$

Thus only 4.12 mol of Ti can be formed.

4. To calculate the mass of titanium metal that can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

https://chem.libretexts.org/@go/page/36992

$$moles\,Ti = mass\,Ti \times molar\,mass\,Ti = 4.12\,mol\,Ti \times \frac{47.867\,g\,Ti}{1\,mol\,Ti} = 197\,g\,Ti \tag{4.4.10}$$

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:

$$TiCl_4: \frac{5.272\,mol\,(actual)}{1\,mol\,(stoich)} = 5.272 \quad Mg: \frac{8.23\,mol\,(actual)}{2\,mol\,(stoich)} = 4.12 \tag{4.4.11}$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

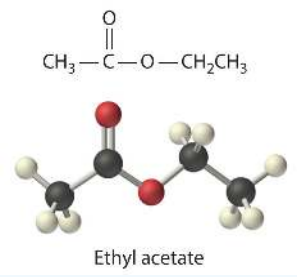
Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 4.4.1 demonstrates.



Determining the Limiting Reactant and Theoretical Yield for a Reaction: https://youtu.be/HmDm1qpNUD0

Example 4.4.1: Fingernail Polish Remover

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.



Ethyl acetate

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 Always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O(l) \tag{4.4.12}$$

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 that the density of a substance is the mass divided by the volume:

$$density = \frac{mass}{volume} \tag{4.4.13}$$

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):

$$moles\, C_2H_5OH = \frac{mass\, C_2H_5OH}{molar\, mass\, C_2H_5OH} \tag{4.4.14}$$

$$= \frac{volume\, C_2H_5OH \times density\, C_2H_5OH}{molar\, mass\, C_2H_5OH} \tag{4.4.15}$$

$$= 10.0\, ml\, C_2H_5OH \times \frac{0.7893\, g\, C_2H_5OH}{1\, ml\, C_2H_5OH} \times \frac{1\, mole\, C_2H_5OH}{46.07\, g\, C_2H_5OH} \tag{4.4.16}$$

$$= 0.171\, mol\, C_2H_5OH \tag{4.4.17}$$

$$moles\, CH_3CO_2H = \frac{mass\, CH_3CO_2H}{molar\, mass\, CH_3CO_2H} \tag{4.4.18}$$

$$= \frac{volume\, CH_3CO_2H \times density\, CH_3CO_2H}{molar\, mass\, CH_3CO_2H} \tag{4.4.19}$$

$$= 10.0\, ml\, CH_3CO_2H \times \frac{1.0492\, g\, CH_3CO_2H}{1\, ml\, CH_3CO_2H} \times \frac{1\, mol\, CH_3CO_2H}{60.05\, g\, CH_3CO_2H} \tag{4.4.20}$$

$$= 0.175\, mol\, CH_3CO_2H \tag{4.4.21}$$

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:

$$moles\, ethyl\, acetate = molethanol \times \frac{1\, mol\, ethyl\, acetate}{1\, mol\, ethanol} \tag{4.4.22}$$

$$= 0.171\, mol\, C_2H_5OH \times \frac{1\, mol\, CH_3CO_2C_2H_5}{1\, mol\, C_2H_5OH} \tag{4.4.23}$$

$$= 0.171\, mol\, CH_3CO_2C_2H_5 \tag{4.4.24}$$

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:

$$mass\, of\, ethyl\, acetate = moleethyl\, acetate \times molar\, mass\, ethyl\, acetate \tag{4.4.25}$$

$$= 0.171\, mol\, CH_3CO_2C_2H_5 \times \frac{88.11\, g\, CH_3CO_2C_2H_5}{1\, mol\, CH_3CO_2C_2H_5} \tag{4.4.26}$$

$$= 15.1\, g\, CH_3CO_2C_2H_5 \tag{4.4.27}$$

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/cm3) to determine the volume of ethyl acetate that could be produced:

$$volume\, of\, ethyl\, acetate = 15.1\, g\, CH_3CO_2C_2H_5 \times \frac{1\, ml\, CH_3CO_2C_2H_5}{0.9003\, g\, CH_3CO_2C_2H_5} \tag{4.4.28}$$

$$= 16.8\,ml\,CH_3CO_2C_2H_5 \tag{4.4.29}$$

Exercise 4.4.1

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

Limiting Reactants in Solutions

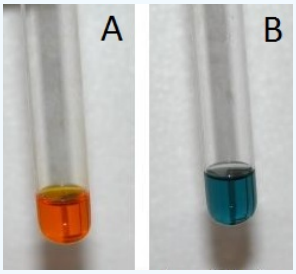
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 4.4.2.

Example

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:

$$3CH_3CH_2OH(aq) + \underset{yellow-orange}{2Cr_2O_7^{2-}}(aq) + 16H^+(aq) \xrightarrow[H_2SO_4(aq)]{Ag^+} 3CH_3CO_2H(aq) + \underset{green}{4Cr^{3+}}(aq) + 11H_2O(l) \tag{4.4.30}$$

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 reaction with a test tube 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 can be used 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 8.5×10^{-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

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol\ Cr_2O_7^{2-}})\left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol\ Cr_2O_7^{2-}}}\right) = 3.9 \times 10^{-6}\ mol\ C_2H_5OH$$

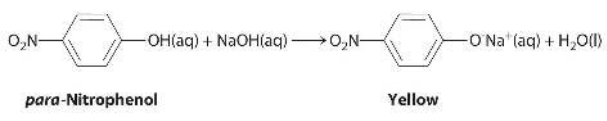
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ C_2H_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ C_2H_5OH})\left(\frac{46.07\ g}{\cancel{mol\ C_2H_5OH}}\right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

Thus 1.8×10^{-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 4.4.2

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 7.20×10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer: 4.93×10^{-5} L or 49.3 μL

In Examples 4.4.1 and 4.4.2, the identities of the limiting reactants are apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, it can be determined by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation. The only difference is that the volumes and concentrations of solutions of reactants, rather than the masses of reactants, are used to calculate the number of moles of reactants, as illustrated in Example 4.4.3.

✓ Example 4.4.3

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 4.4.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7 \tag{4.4.31}$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3 \tag{4.4.32}$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$K_2Cr_2O_7:\ \frac{0.085\ mol}{1\ mol} = 0.085 \tag{4.4.33}$$

$$AgNO_3:\ \frac{0.14\ mol}{2\ mol} = 0.070 \tag{4.4.34}$$

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, convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7 \tag{4.4.35}$$

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 4.4.3

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



Limiting Reactant Problems Using Molarities: https://youtu.be/eOXTliL-gNw

Summary

- The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained.

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.

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4.5: Other Practical Matters in Reactions

Learning Objectives

- To understand the concept of quantify incomplete reactions, including sequential and parallel reactions.

Theoretical Yields

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, the amount obtained if the reaction occurred perfectly and the purification method were 100% efficient.

In reality, less product is always obtained 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 run to completion, resulting in a mixture of products and reactants; this last possibility is a common occurrence. Therefore, the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$percent\ yield = \frac{actual\ yield\ (g)}{theoretical\ yield\ (g)} \times 100 \tag{4.5.1}$$

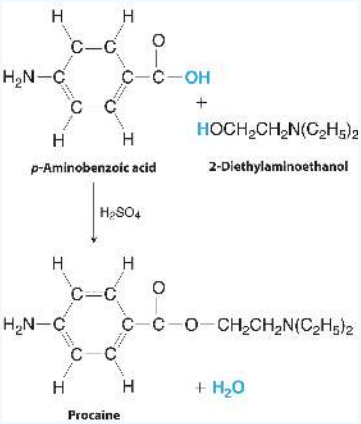
The method used to calculate the percent yield of a reaction is illustrated in Example 4.5.1.

Example 4.5.1: Novocain

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 H2SO4 (indicated above the arrow) by the reaction

$$\underset{p-aminobenzoic\ acid}{C_7H_7NO_2} + \underset{2-diethylaminoethanol}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{procaine}{C_{13}H_{20}N_2O_2} + H_2O \tag{4.5.1}$$

If this reaction was carried out using 10.0 g of p-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and 15.7 g of procaine were isolated, what is 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:

$$moles\, p-aminobenzoic\, acid = 10.0\, g \times \frac{1\, mol}{137.14\, g} = 0.0729\, mol\, p-aminbenzoic\, acid \tag{4.5.2}$$

$$moles\, 2-diethylaminoethanol = 10.0\, g \times \frac{1\, mol}{117.19\, g} = 0.0853\, mol\, 2-diethylaminoethanol \tag{4.5.3}$$

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 (C13H20N2O2) to calculate its molar mass, which is 236.31 g/mol.

$$theoretical\, yield\, of\, procaine = 0.0729\, mol \times \frac{236.31\, g}{1\, mol} = 17.2\, g \tag{4.5.4}$$

C The actual yield was only 15.7 g of procaine, so the percent yield is

$$percent\, yield = \frac{15.7\, g}{17.2\, g} \times 100 = 91.3\% \tag{4.5.5}$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

? Exercise 4.5.1: Extraction of Lead

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:

$$2PbS_{(s)} + 3O_2 \rightarrow 2PbO_{(s)} + 2SO_{2(g)} \tag{4.5.6}$$

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:

$$PbO_{(s)} + C_{(s)} \rightarrow Pb_{(l)} + CO_{(g)} \tag{4.5.7}$$

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?



Figure used with permission from Wikipedia.

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 the chemist 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 the unlikelihood of a 100% yield. 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.

Consecutive Reactions, Simultaneous Reactions, and Overall Reactions

Most of time it takes more than one steps to get desired product. Two more complex reactions are the consecutive and simultaneous reactions. Reactions that are carried out one after another in sequence to yield a final product are called consecutive reactions (e.g., occurring sequenceally):

$$A \rightarrow Y \rightarrow Z \tag{4.5.2}$$

Any substance that is produced in one step and is consumed in another step of a multistep process is called an *intermediate* (e.g., Y in Equation 4.5.2). The *Overall Reaction* is the chemical equation that expresses all the reactions occurring in a single overall equation.

Example 4.5.2:Purification of TiO_2

Step 1:

$$2TiO2_{(\text{impure solid})} + 3C_{(s)} + 4Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + CO_{2(g)} + 2CO_{(g)} \tag{4.5.8}$$

Step 2:

$$2 \times [TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)}] \tag{4.5.9}$$

Overall:

$$3C_{(s)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2CO_{(g)} \tag{4.5.10}$$

$TiCl_4$ is an intermediate in this reaction

Example 4.5.3

How many gram of $NaBr$ is produced if 55.85g of Fe is consumed the the following series of reactions?

$$3Fe + 3Br_2 \rightarrow 3FeBr_2 \tag{4.5.11}$$

$$3FeBr_2 + Br_2 \rightarrow Fe_3Br_8 \tag{4.5.12}$$

$$Fe_3Br_8 + 4Na_2CO_3 \rightarrow 8NaBr + 4CO_2 + Fe_3O_4 \tag{4.5.13}$$

Overall reaction:

$$3Fe + 4Br_2 + 4Na_2CO_3 \rightarrow 8NaBr + 4CO_2 + Fe_3O_4 \tag{4.5.14}$$

Solution

under construction

In simultaneous reactions, two or more substances react independently of one another in separate reactions occurring simultaneously

$$A \rightarrow Y \tag{4.5.3a}$$

and

$$B \rightarrow B \tag{4.5.3b}$$

Equations 4.5.3 involve two reactions evolving in parallel, however sometimes there exist a coupling between the two (or more) reactions with shared reactant, intermediates or products. is competition involved, like in the scheme:

$$A + B \rightarrow Y \tag{4.5.4a}$$

and

$$A + C \rightarrow Z \tag{4.5.3b}$$

In the above simultaneous reaction, both B and C compete with each another for reacting A. This is superficially similar to a common ion effect.

Example 4.5.4: Oxidation of Magnalium

Magnalium is an aluminum alloy with magnesium that exhibits greater strength, greater corrosion resistance, and lower density than pure aluminum. How many grams of $H_{2(g)}$ are generated if a 0.710 g piece of magnalium (with a 70% Al and 30.0% Mg by mass composition) with excess $HCl_{(aq)}$?

Solution

under construction

Summary

- The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained.

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.

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CHAPTER OVERVIEW

5: Reactions in Aqueous Solutions

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This chapter introduces techniques for preparing and analyzing aqueous solutions, for balancing equations that describe reactions in solution, and for solving problems using solution stoichiometry. By the time you complete this chapter, you will know enough about aqueous solutions to explain what causes acid rain, why acid rain is harmful, and how a Breathalyzer measures alcohol levels. You will also understand the chemistry of photographic development, be able to explain why rhubarb leaves are toxic, and learn about a possible chemical reason for the decline and fall of the Roman Empire.

Topic hierarchy

5.1: The Nature of Aqueous Solutions
5.2: Precipitation Reactions
5.3: Acid–Base Reactions
5.4: Principles of Oxidation-Reduction Reactions
5.5: Balancing Oxidation-Reduction Reactions
5.6: Oxidizing and Reducing Agents
5.7: Quantitative Analysis Using Titration

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5.1: The Nature of 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 5.1.1, 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 δ^+. 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 in which one portion of the molecule carries a partial negative charge, while the other portion carries a partial positive charge (Figure 5.1.1). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

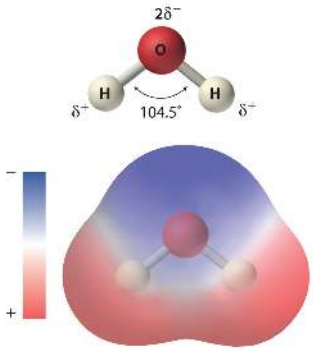


Figure 5.1.1: The Polar Nature of Water. *Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) and the hydrogen atoms are partially positively charged (δ^+; 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 (Figure 5.1.2). 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!

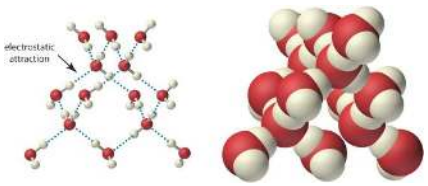


Figure 5.1.2: The Structure of Liquid Water. Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule and the 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 previously,, 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 5.1.3). 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.

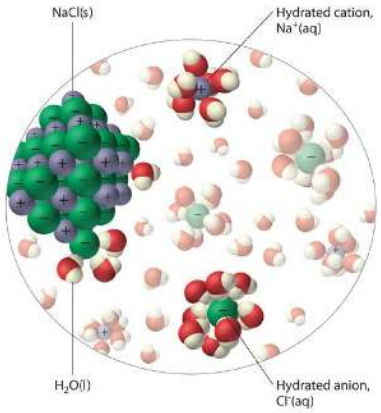


Figure 5.1.3: The Dissolution of Sodium Chloride in Water. *An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.*

Note

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 5.1.4). 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 5.1.4 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

Solutions that contain ions conduct electricity.

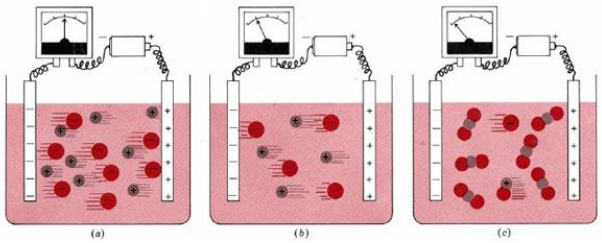


Figure used with permission from ChemePrime.

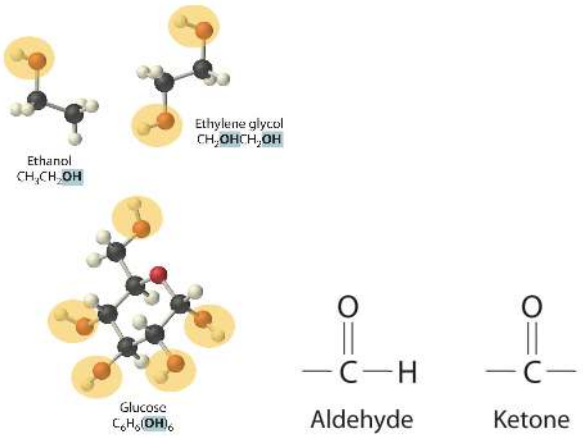
An electrolyte is any compound that can form ions when dissolved in water (c.f. nonelectrolytes). Electrolytes may be strong or weak. is any compound that can form ions when it dissolves in water. When strong electrolytes dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure 5.1.4). Examples include ionic compounds such as barium chloride ($BaCl_2$) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

$$BaCl_2(s) \xrightarrow{H_2O(l)} Ba^{2+}(aq) + 2Cl^-(aq)$$

BaCl_2 (s) \xrightarrow{H_2O(l)} Ba^{2+} (aq) + 2Cl^- (aq) \label{5.1.2}

The single arrows from reactant to products in Equation 5.1.2 and Equation 5.1.3 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 elsewhere.



General structure of an aldehyde and a ketone. *Notice that both contain the C=O group.*

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. The topic of why alcohols and carboxylic acids behave differently in aqueous solution is for a different Module; 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. The distinctions between soluble and insoluble substances and between strong, weak, and nonelectrolytes are illustrated in Figure 5.1.5.

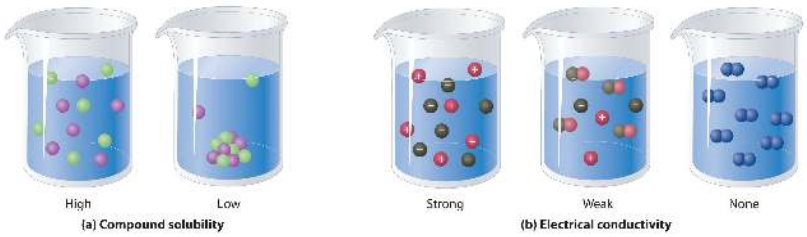


Figure 5.1.5: The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b). *When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated with 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.*

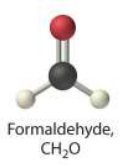
Note

Ionic substances and carboxylic acids are electrolytes; alcohols, aldehydes, and ketones are nonelectrolytes.

Example 5.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. formaldehyde



b. 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 5.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. $(CH_3)_2CHOH$ (2-propanol)



b. ammonium sulfate

Answer

a. nonelectrolyte
b. strong electrolyte



Predicting the Solubility of Ionic Compounds: https://youtu.be/U3QNwnfmvGU

Summary

- Aqueous solutions can be classified as polar or nonpolar depending on how well they conduct electricity.

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.

Contributors and Attributions

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5.2: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubilities.

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. 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:

$$AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq) \tag{5.2.1}$$

This equation has the general form of an exchange reaction:

$$AC + BD \rightarrow \underset{insoluble}{AD} + BC \tag{5.2.2}$$

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.



***Video**: Mixing Potassium Chromate and Silver Nitrate together to initiate a precipitation reaction (Equation 5.2.3).*

While chemical equations show 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. When aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall balanced chemical equation for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq) \tag{5.2.3}$$

Although Equation 5.2.3 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:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq) \tag{5.2.4}$$

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:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{5.2.5}$$

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 5.2.5, 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:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{5.2.6}$$

The complete ionic equation for this reaction is as follows:

$$2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq) \tag{5.2.7}$$

Because two NH_4^+(aq) and two F^-(aq) ions appear on both sides of Equation 5.2.7, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 5.2.8), which is identical to Equation 5.2.5:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{5.2.8}$$

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 5.2.1

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 5.2.1: Mixing Silver Fluoride with Sodium Phosphate

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 (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.



Determining the Products for Precipitation Reactions: https://youtu.be/r0kYeZVuTAM

Predicting Solubilities

Table 5.2.2 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 5.2.2 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 later, 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 5.2.2: 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**

	Soluble		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 5.2.1).

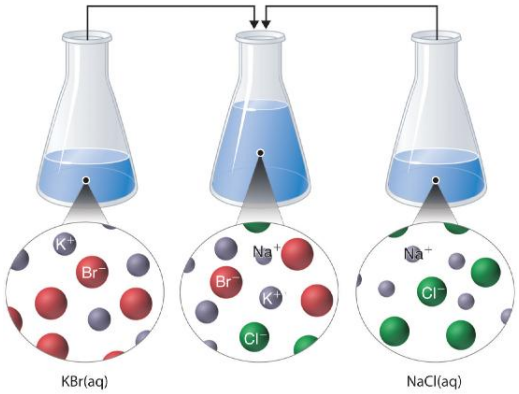


Figure 5.2.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Example 5.2.2

Using the information in Table 5.2.2, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

a. Aqueous solutions of barium chloride and lithium sulfate are mixed.
b. Aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.
c. Aqueous solutions of strontium bromide and aluminum nitrate are mixed.
d. Solid lead(II) acetate is added to an aqueous solution of ammonium iodide.

Given: reactants

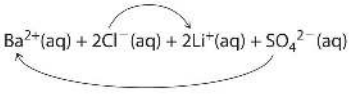
Asked for: reaction and net ionic equation

Strategy:

A. Identify the ions present in solution and write the products of each possible exchange reaction.
B. Refer to Table 5.2.2 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:

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 $BaSO_4$:



B We now need to decide whether either of these products is insoluble. Table 5.2.2 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

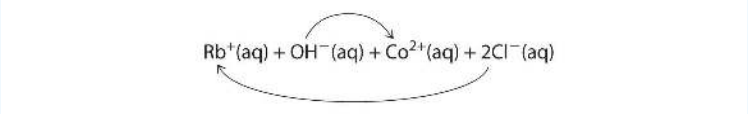
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) \tag{5.2.9}$$

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.

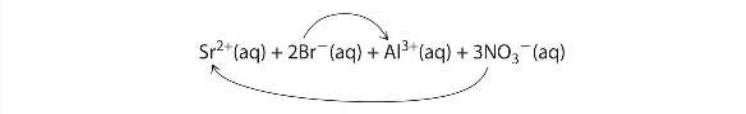
1. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+, OH^-, Co^{2+}, and Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



B According to Table 5.2.2, 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:

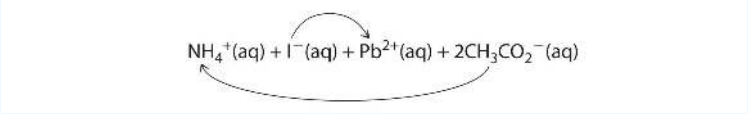
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

2. **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 5.2.2, both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

1. **A** According to Table 5.2.2, 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 5.2.2, 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 5.2.2

Using the information in Table 5.2.2, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer

a. $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
b. $2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$
c. $NaF(s)$ dissolves; no net reaction
d. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

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.

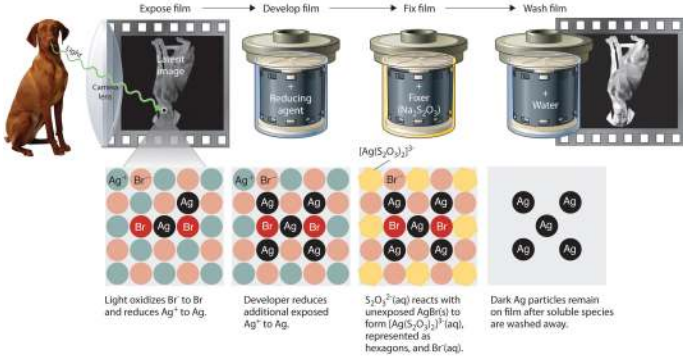


Figure 5.2.2: Outline of the Steps Involved in Producing a Black-and-White Photograph

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 5.2.2. 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.

✔ Example 5.2.3

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:

$$moles\ AgCl = \frac{grams\ AgCl}{molar\ mass\ AgCl} = 3.73\ \cancel{g\ AgCl}\left(\frac{1\ mol\ AgCl}{143.32\ \cancel{g\ AgCl}}\right) = 0.0260\ mol\ AgCl \tag{5.2.10}$$

Therefore, the 500 mL sample of the solution contained 0.0260 mol of Ag^+. The Ag^+ concentration is determined as follows:

$$[Ag^+] = \frac{moles\ Ag^+}{liters\ soln} = \frac{0.0260\ mol\ AgCl}{0.500\ L} = 0.0520\ M \tag{5.2.11}$$

B The total number of moles of Ag^+ present in 1500 L of solution is as follows:

$$moles\ Ag^+ = 1500\ \cancel{L}\left(\frac{0.520\ mol}{1\ \cancel{L}}\right) = 78.1\ mol\ Ag^+ \tag{5.2.12}$$

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

$$mass\ NaCl = 78.1\ \cancel{mol\ NaCl}\left(\frac{58.44\ g\ NaCl}{1\ \cancel{mol\ NaCl}}\right) = 4560\ g\ NaCl = 4.56\ kg\ NaCl \tag{5.2.13}$$

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 5.2.3

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%

Note

Precipitation reactions are a subclass of double displacement reactions.



Determining the Net Ionic Equation for a Precipitation Reaction: https://youtu.be/AMJz1Sdz8IA

Summary

A complete ionic equation consists of the net ionic equation and spectator ions. Predicting the solubility of ionic compounds in water can give insight into whether or not a reaction will occur. 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.

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.

Contributors and Attributions

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5.3: Acid–Base Reactions

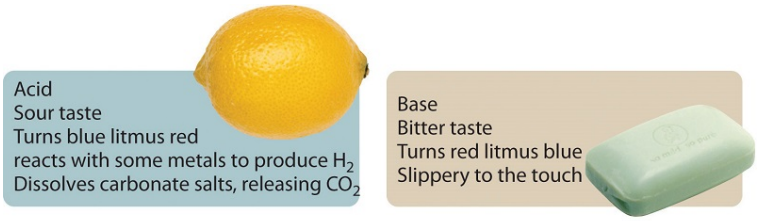
Learning Objectives

- 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

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.



Although we include their tastes among the common characteristics of acids and bases, we never advocate tasting an unknown chemical!

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 5.3.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 5.3.2):

$$\underset{an\ Arrhenius\ acid}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{5.3.1}$$

$$\underset{an\ Arrhenius\ base}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{5.3.2}$$

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 5.3.3) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{5.3.3}$$

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 5.3.3, 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.



Definitions of Acids and Bases: https://youtu.be/r8reN0CSIHw

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^+. 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), (Equations 5.3.4, 5.3.5, and 5.3.6):

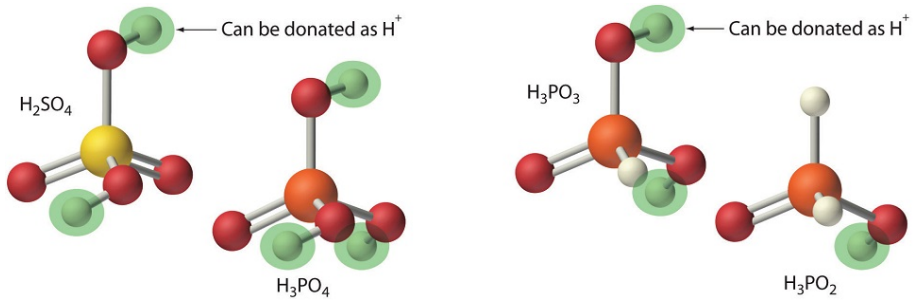
$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{5.3.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{5.3.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{5.3.6}$$

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:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{5.3.7}$$

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 8.1. Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 5.3.8) but a weak acid when it donates its second proton (Equation 5.3.9) as indicated by the single and double arrows, respectively:

$$\underset{strong\ acid}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{5.3.8}$$

$$\underset{weak\ acid}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{5.3.9}$$

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:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{5.3.10}$$

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-}).

> *There is no correlation between the solubility of a substance and whether it is a strong electrolyte, a weak electrolyte, or a nonelectrolyte.*

Table 5.3.1 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.

Table 5.3.1: *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 5.3.1

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

a. $CH_3CH_2CO_2H$
b. CH_3OH
c. $Sr(OH)_2$
d. $CH_3CH_2NH_2$
e. $HBrO_4$

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:

a. **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.
b. **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.
c. **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 $Ca(OH)_2$.
d. **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 5.3.7), reacting with water to produce small amounts of the OH^- ion. Ethylamine is therefore a weak base.
e. **A** $HBrO_4$ is perbromic acid, an inorganic compound. **B** It is not listed in Table 5.3.1 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 5.3.1

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

a. $Ba(OH)_2$
b. HIO_4
c. $CH_3CH_2CH_2CO_2H$
d. $(CH_3)_2NH$
e. CH_2O

Answer

a. strong base
b. strong acid
c. weak acid
d. weak base
e. none of these; formaldehyde is a neutral molecule



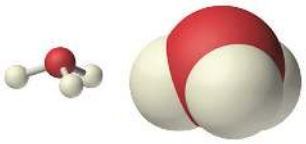
Definition of Strong/Weak Acids & Bases: https://youtu.be/gN2l8H_AWGU

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:

$$\underset{acid\ (proton\ donor)}{H_2SO_4(l)} + \underset{base\ (proton\ acceptor)}{H_2O(l)} \rightarrow \underset{acid}{H_3O^+}(aq) + \underset{base}{HSO_4^-}(aq) \tag{5.3.11}$$

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 ion and is 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 5.3.7) with the understanding that the product is actually the$H_3O^+_{(aq)}$ ion.



Hydronium ion, H_3O^+

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:

$$\underset{base}{NH_3(g)} + \underset{acid}{H_2O(l)} \rightleftharpoons \underset{acid}{NH_4^+(aq)} + \underset{base}{OH^-(aq)} \tag{5.3.12}$$

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 5.3.11, 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 5.3.12, the products are NH_4^+, an acid, and OH^-, a base. The product NH_4^+ is called the conjugate acid 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 pairs. 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 5.3.12, 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:

$$\underset{acid}{HBr(aq)} + \underset{base}{NaOH(aq)} \rightarrow \underset{water}{H_2O(l)} + \underset{salt}{NaBr(aq)} \tag{5.3.13}$$

> *Acid plus base yields water plus salt.*

If we write the complete ionic equation for the reaction in Equation 5.3.13, we see that $Na^+_{(aq)}$ and $Br^-_{(aq)}$ are spectator ions and are not involved in the reaction:

$$H^+(aq) + \cancel{Br^-(aq)} + \cancel{Na^+(aq)} + OH^-(aq) \rightarrow H_2O(l) + \cancel{Na^+(aq)} + \cancel{Br^-(aq)} \tag{5.3.14}$$

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:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{5.3.15}$$

The net ionic equation for the reaction of any strong acid with any strong base is identical to Equation 5.3.15.

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:

$$\underset{strong\ acid}{HCl(aq)} + \underset{weak\ base}{NH_3(aq)} \rightarrow \underset{salt}{NH_4Cl(aq)} \tag{5.3.16}$$

$$\underset{weak\ acid}{CH_3CO_2H(aq)} + \underset{strong\ base}{NaOH(aq)} \rightarrow \underset{salt}{CH_3CO_2Na(aq)} + H_2O(l) \tag{5.3.17}$$

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:

$$\underset{weak\ acid}{CH_3CO_2H(aq)} + \underset{weak\ base}{NH_3(aq)} \rightarrow \underset{salt}{CH_3CO_2NH_4(aq)} \tag{5.3.18}$$

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.

Note

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:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \tag{5.3.19}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l) \tag{5.3.20}$$

$$CN^-(aq) + H^+(aq) \rightarrow HCN(g) \tag{5.3.21}$$

$$S^{2-}(aq) + H^+(aq) \rightarrow HS^-(aq) \tag{5.3.22}$$

$$HS^-(aq) + H^+(aq) \rightarrow H_2S(g) \tag{5.3.23}$$

The reactions in Equations 5.3.19-5.3.22 are responsible for the rotten egg smell that is produced when metal sulfides come in contact with acids.



Acid/Base Neutralization Reactions & Net Ionic Equations: https://youtu.be/gDS93ySeF80

Example 5.3.2: Calcium Propionate

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 5.3.2

Write a balanced chemical equation for the reaction of solid sodium acetate with dilute sulfuric acid to give sodium sulfate.

Answer:

$$2CH_3CO_2Na(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CH_3CO_2H(aq)$$

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.



Stomach acid. An antacid tablet reacts with 0.1 M HCl (the approximate concentration found in the human stomach).

✓ Example 5.3.3

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 $\dfrac{0.0070\ \cancel{mol\ CaCO_3}}{0.00500\ \cancel{mol\ CaCO_3}} = 1.4$ Tums tablets.

? Exercise 5.3.3

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 scale 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:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{5.3.24}$$

The concentration of hydrogen ions in pure water is only 1.0×10^{-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 1.0×10^{-7} M. Pure water is a neutral solution in which the total positive charge from all the cations is matched by an identical total negative charge from all the anions. At room temperature this is $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M.

The pH scale describes the hydrogen ion concentration of a solution in a way that avoids the use of exponential notation. The negative base-10 logarithm of the hydrogen ion concentration: pH is often 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.

$$pH = -log[H^+] \tag{5.3.25}$$

Conversely,

$$[H^+] = 10^{-pH} \tag{5.3.26}$$

(If you are not familiar with logarithms or using a calculator to obtain logarithms and antilogarithms)

Because the hydrogen ion concentration is 1.0×10^{-7} M in pure water at 25°C, the pH of pure liquid water (and, by extension, of any neutral solution) is

$$pH = -\log[1.0 \times 10^{-7}] = 7.00 \tag{5.3.27}$$

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 5.3.15. 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:

$$pH = -\log[1.0] = 0.00 \tag{5.3.28}$$

Note

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

$$pH = -log[1.0 \times 10^{-14}] = 14.00 \tag{5.3.29}$$

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 5.3.2.

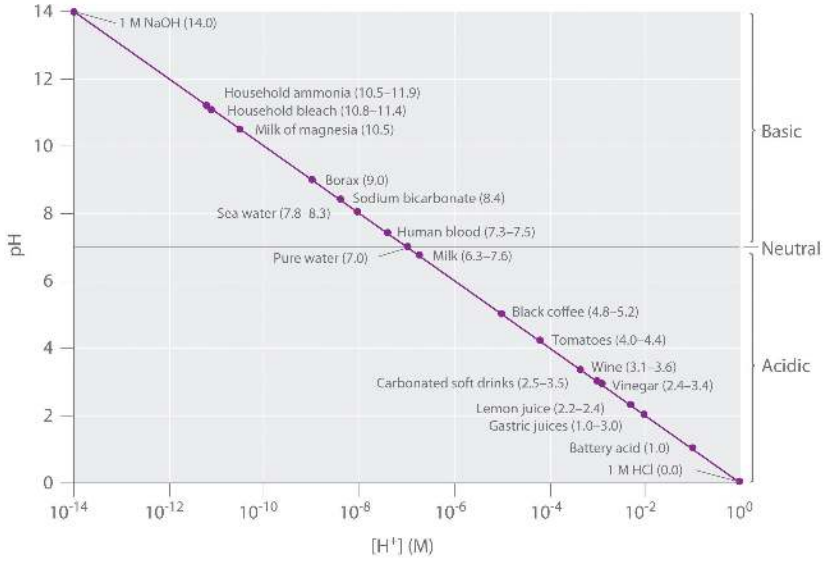


Figure 5.3.2 A Plot of pH versus $[H^+]$ for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 5.3.4

a. What is the pH of a 2.1×10^{-2} M aqueous solution of $HClO_4$?
b. 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 5.3.25 or 5.3.24, determine $[H^+]$ and convert it to pH or vice versa.

Solution:

a. $HClO_4$ (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.

b. We are given the pH and asked to calculate the hydrogen ion concentration. From Equation 5.3.24,

$$10^{-pH} = [H^+]$$

Thus $[H^+] = 10^{-3.80} = 1.6 \times 10^{-4}\ M$.

Exercise 5.3.4

a. What is the pH of a 3.0×10^{-5} M aqueous solution of HNO_3?
b. What is the hydrogen ion concentration of turnip juice, which has a pH of 5.41?

Answer

a. $pH = 4.52$
b. $[H^+] = 3.9 \times 10^{-6}\ M$

Tools have been developed that make the measurement of pH simple and convenient (Figures 5.3.3 and 5.3.4). For example, pH paper consists of strips of paper impregnated with one or more acid–base indicators, 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 5.3.4).



Figure 5.3.3: These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. Photo by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).



Figure 5.3.4: These three meters and probes can measure pH (left) and electrical conductivity (center and right). The image can be enlarged if you click on it. Photo by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).



Introduction to pH: https://youtu.be/pQOa3bb5YEE

Summary

An acidic solution and a basic solution react together in a neutralization reaction that also forms a salt. 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 1×10^{-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.

Contributors and Attributions

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5.4: Principles of Oxidation-Reduction Reactions

Learning Objectives

- To identify oxidation–reduction reactions in solution.

The term oxidation 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

Any oxidation must **ALWAYS** be accompanied by a reduction and vice versa.

Originally, the term reduction 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:

$$Cu_2O(s) + H_2(g) \rightarrow 2Cu(s) + H_2O(g) \tag{5.4.1}$$

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 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

$$4Al(s) + 3O_2 \rightarrow 2Al_2O_3(s) \tag{5.4.2}$$

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):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^{3+} + 6O^{2-} \tag{5.4.3}$$

Equation 5.4.1 and Equation 5.4.2 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 5.4.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$electrons\,lost = 4\ Al\ atoms \times \frac{3\ e^-\ lost}{Al\ atom} = 12\ e^-\ lost \tag{5.4.4}$$

electrons \, gained = 6 \, O \, atoms \times {2 \, e^- \, gained \over O \, atom} = 12 \, e^- \, gained \label{5.4.4a}

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained.

An additional example of a redox reaction, the reaction of sodium metal with oxygen in air, is illustrated in Figure 5.4.1.

Note

In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.



Redox Reactions: https://youtu.be/1v3yaaR_nHc

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. Previosuly, 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 5.4.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

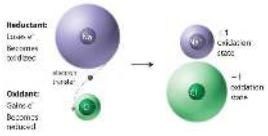


Figure 5.4.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

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.

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.

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 will discover in Chapter 6. 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.

The reduction of copper(I) oxide shown in Equation 5.4.5 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:

$$\overset{+1}{Cu}_2\overset{-2}{O}(s) + \overset{0}{H}_2(g) \rightarrow 2\overset{0}{Cu}(s) + \overset{+1}{H}_2\overset{-2}{O}(g) \tag{5.4.5}$$

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:

$$electrons\,lost = 2\,H\,atoms \times \frac{1\,e^-\,lost}{H\,atom} = 2\,e^-\,lost \tag{5.4.6}$$

$$electrons\,gained = 2\,Cu\,atoms \times \frac{1\,e^-\,gained}{Cu\,atom} = 2\,e^-\,gained \tag{5.4.7}$$

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 5.4.1

Assign oxidation states to all atoms in each compound.

a. sulfur hexafluoride (SF_6)
b. methanol (CH_3OH)
c. ammonium sulfate [$(NH_4)2SO_4$]
d. magnetite (Fe_3O_4)
e. 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:

a. 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

b. 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

c. 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 2.4). 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:

$$[(4\text{ H atoms})(+1)] + [(1\text{ N atom})(−3)] = +1, \text{ the charge on the } NH_4^+ \text{ ion}$$

For SO42−, oxygen has an oxidation state of −2 (rule 5), so sulfur must have an oxidation state of +6:

$$[(4\text{ O atoms})\ (−2)] + [(1\text{ S atom})(+6)] = −2, \text{ the charge on the sulfate ion}$$

d. 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:

$$[(4\text{ O atoms})(−2)]+[(3\text{ Fe atoms})\left(+\tfrac{8}{3}\right)]= 0$$

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."

e. 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

$$[(4\text{ H atoms})(+1)] + [(2\text{ O atoms})(−2)] = 0$$

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

$$[(2\text{ O atoms})(−2)] + [(1\text{ H atom})(+1)] = −3$$

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

$$\overset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\overset{-2}{O_2}\overset{+1}{H} \tag{5.4.8}$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

? Exercise 5.4.1

Assign oxidation states to all atoms in each compound.

a. barium fluoride (BaF_2)
b. formaldehyde (CH_2O)
c. potassium dichromate ($K_2Cr_2O_7$)
d. cesium oxide (CsO_2)
e. ethanol (CH_3CH_2OH)

Answer:

a. Ba, +2; F, −1
b. C, 0; H, +1; O, −2
c. K, +1; Cr, +6; O, −2

d. Cs, +1; O, −½
e. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

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 5.4.1). 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) \label{5.4.5}

In subsequent steps, $FeCl_2$ undergoes oxidation to form a reddish-brown precipitate of $Fe(OH)_3$.



Figure 5.4.2: 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

Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \label{5.4.5}

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:

Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \label{5.4.5}

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 5.4.8) and the reduction of silver salts by copper (Equation 5.4.9 and Figure 5.4.2):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s) \tag{5.4.9}$$

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \tag{5.4.10}$$

The reaction in Equation 5.4.8 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 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, 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:

$$Zn(s) + Mg^{2+}(aq) \not\rightarrow Zn^{2+}(aq) + Mg(s) \tag{5.4.11}$$

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s) \tag{5.4.12}$$

Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure 5.4.4), 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, which have the greatest tendency to be oxidized. (located at the top of the series) and which are inert metals, which have the least tendency to be oxidized. (at the bottom of the series).

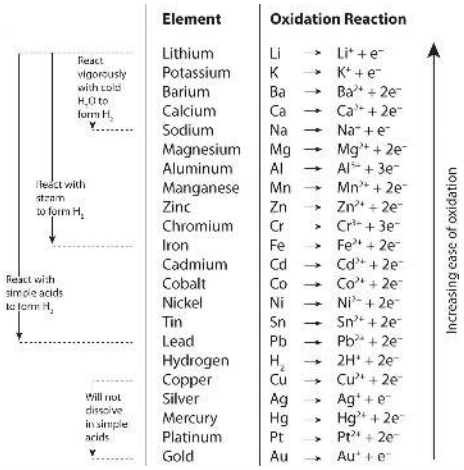


Figure 5.4.4: The Activity Series

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 5.4.4, 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 5.4.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

Example 5.4.2

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 .5.4.4 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:

$$Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s) \tag{5.4.13}$$

   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:

$$Pb(s) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + H_2(g) \tag{5.4.14}$$

   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 5.4.2

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

- Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation.

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 5.4.1), 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 5.4.4), 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.

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5.5: Balancing Oxidation-Reduction Reactions

The Learning Objectives of this Module are:

1. To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions already. 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

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5.6: Oxidizing and Reducing Agents

Compounds that are capable of accepting electrons, such as O_2 or F_2, are called oxidants (or oxidizing agents) 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) 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 3.30:

$$\text{oxidant + reductant} \rightarrow \text{oxidation−reduction}$$

$$\underset{gains\ e^-\ (is\ reduced)}{O_2(g)} + \underset{loses\ e^-\ (is\ oxidized)}{4Na(s)} \rightarrow \underset{redox\ reaction}{2\ Na_2O(s)} \tag{3.30}$$

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 reaction, first introduced in Section 3.2 "Determining Empirical and Molecular Formulas", 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 3.9 "An Example of a Combustion Reaction". 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:

$$\overset{+1}{\underset{-2}{C_6H_{12}}} + 9\overset{0}{O_2} \rightarrow 6\overset{+4}{\underset{-2}{CO_2}} + 6\overset{+1}{\underset{-2}{H_2O}} \tag{3.31}$$

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.

We described the defining characteristics of oxidation–reduction, or redox, reactions in Chapter 7. 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

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.

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5.7: Quantitative Analysis Using Titration

The Learning Objective of this Module is 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 analysis (A 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 point (The 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.

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CHAPTER OVERVIEW

Unit III: Physical Properties of Gases

Here, we explore the relationships among pressure, temperature, volume, and the amount of gases. You will learn how to use these relationships to describe the physical behavior of a sample of both a pure gaseous substance and mixtures of gases. By the end of this chapter, your understanding of the gas laws and the model used to explain the behavior of gases will allow you to explain how straws and hot-air balloons work, why hand pumps cannot be used in wells beyond a certain depth, why helium-filled balloons deflate so rapidly, and how a gas can be liquefied for use in preserving biological tissue.

6.1: Properties of Gases
6.2: Gas Pressure
6.3: Relationships among Pressure, Temperature, Volume, and Amount
6.4 The Ideal Gas Law
6.5 Mixtures of Gases
6.6: Gas Volumes and Stoichiometry
6.7: Kinetic Molecular Theory of Gases
6.8: Connecting Gas Properties to Kinetic Molecular Theory
6.9: Chapter Problems

Thumbnail: Motion of gas molecules. The randomized thermal vibrations of fundamental particles such as atoms and molecules—gives a substance its "kinetic temperature." Here, the size of helium atoms relative to their spacing is shown to scale under 1950 atmospheres of pressure. (CC BY-SA 3.0; Greg L).

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6.1: Properties of Gases

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 6.1.1 compares the three states of matter and illustrates the differences at the molecular level.

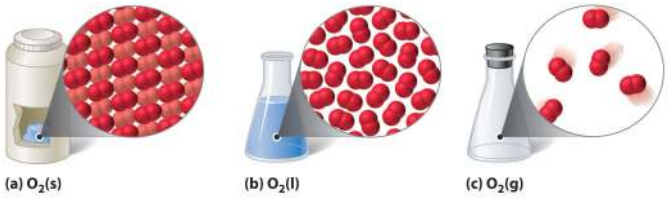


Figure 6.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (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 vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are 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 6.1.1.

Table 6.1.1: 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 6.1.2 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.

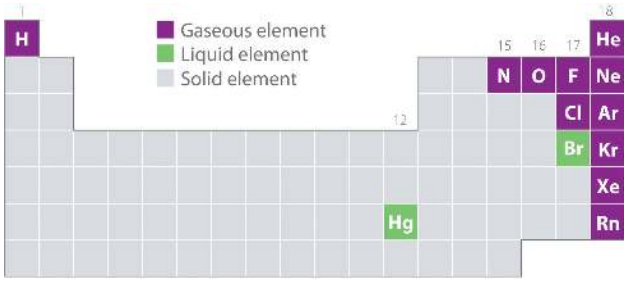


Figure 6.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.



Defining Gas Pressure: https://youtu.be/_CRn3cFs2CI

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).

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6.2: 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 demonstrated below, these variables are *not* independent (i.e., they cannot be arbitrarily be varied). 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) of the gas, the force (F) per unit area (A) of surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{6.2.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 6.2.1 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. 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)**, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{6.2.2}$$

Example 6.2.1

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

a. lying flat?
b. 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 6.2.1 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 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

$$F = ma = 2.00 \text{ kg} \times 9.8067 \frac{\text{m}}{\text{s}^2} = 19.6 \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6 \text{ N}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270 \text{ m} \times 0.210 \text{ m} = 0.0567 \text{ m}^2.$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6 \text{ N}}{0.0567 \text{ m}^2} = 3.46 \times 10^2 \text{Pa}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$\text{A} = 21.0 \text{ cm} \times 4.5 \text{ cm} = 0.210 \text{ m} \times 0.045 \text{ m} = 9.5 \times 10^{-3} \text{ m}^2$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6 \text{ N}}{9.5 \times 10^{-3} \text{ m}^2} = 2.06 \times 10^3 \text{ Pa}$$

? Exercise 6.2.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a

3.27×10^4 Pa

Answer b

5.9×10^6 Pa

Barometric 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 (Figure 6.2.1). Every point on Earth's surface experiences a net pressure called ***barometric pressure***. The pressure exerted by the atmosphere is considerable: a 1 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 101 kPa:

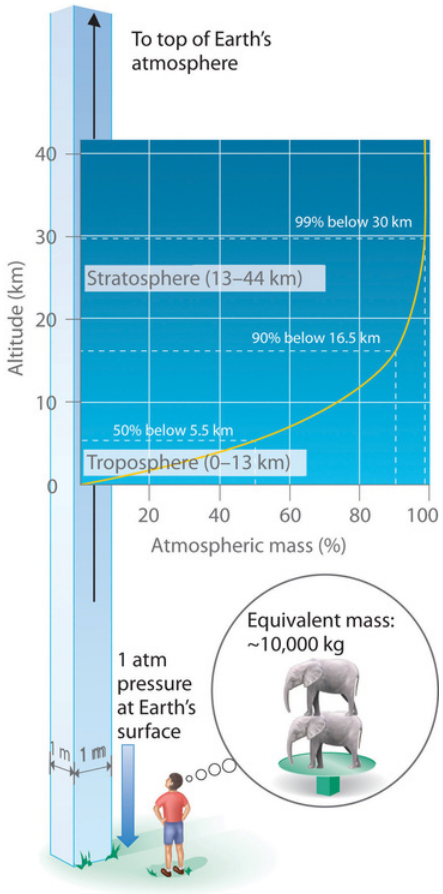


Figure 6.2.1: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

Barometric pressure can be measured using a barometer, 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 6.2.2). 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. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A} \tag{6.2.3}$$

$$= \frac{mg}{A} \tag{6.2.4}$$

$$= \frac{\rho V \cdot g}{A} \tag{6.2.5}$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \tag{6.2.6}$$

$$= \rho g h \tag{6.2.7}$$

with

- g is the gravitational acceleration,
- m is the mass,
- ρ is the density,

- V is the volume,
- A is the bottom area, and
- h is height of the mercury column.

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 6.2.2. 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.

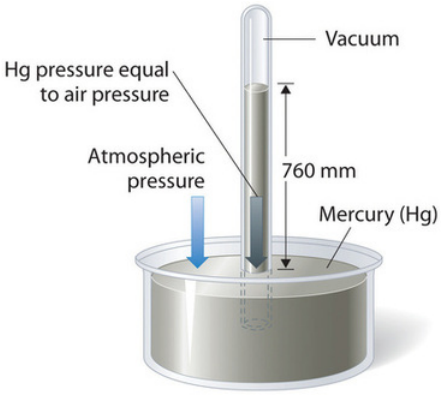


Figure 6.2.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1 \text{ atm} = 760\ mmHg \tag{6.2.8}$$

$$= 760\ torr \tag{6.2.9}$$

$$= 1.01325 \times 10^5\ Pa \tag{6.2.10}$$

$$= 101.325\ kPa \tag{6.2.11}$$

Thus a pressure of 1 atm equals 760 mmHg exactly.

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 barometric 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 barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Example 6.2.2: Barometric Pressure

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 barometric pressure is only 454 mmHg. Convert this pressure to

a. atmospheres (atm).
b. bar.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and bar

Strategy:

Use the conversion factors in Equation 6.2.11 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 6.2.11, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{6.2.12}$$

$$= 0.597 \ atm$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{6.2.13}$$

$$= 0.605 \ bar$$

? Exercise 6.2.2: Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.
b. bar.

Answer a

234 mmHg;

Answer b

0.312 bar

Manometers

Barometers measure barometric pressure, but manometers 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 6.2.3. 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.

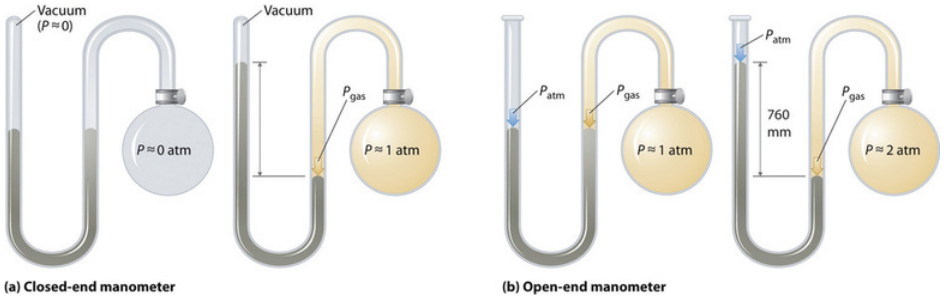


Figure 6.2.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between barometric 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 6.2.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric 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 barometric 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 barometric pressure minus the difference in the heights of the two columns.

Example 6.2.3

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? (The density of water is 1.00 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

$$P = 0.200 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 152 \text{ mmHg}$$

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 to the density of water

$$P = d_{\text{wat}} g h_{\text{wat}} = d_{\text{Hg}} g h_{\text{Hg}}$$

$$h_{\text{wat}} = h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} = 152 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} = 2070 \text{ mm}$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise 6.2.3

Suppose you want to design a barometer to measure barometric 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 6.2.3 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. The 1.00 atm corresponds to a column height of

$$\begin{aligned} h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} \\ &= 760 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} \\ &= 1.03 \times 10^4 \ mm \\ &= 10.3 \ m \end{aligned}$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric 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 barometric 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

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. 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 *barometric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric 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.



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6.3: Relationships among Pressure, Temperature, Volume, and Amount

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (*P*) and its temperature (*T*), volume (*V*), and amount (*n*) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

The Relationship between Pressure and Volume: Boyle's Law

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.

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 6.3.1. 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 6.3.2). 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:

$$PV = \text{constant} \tag{6.3.1}$$

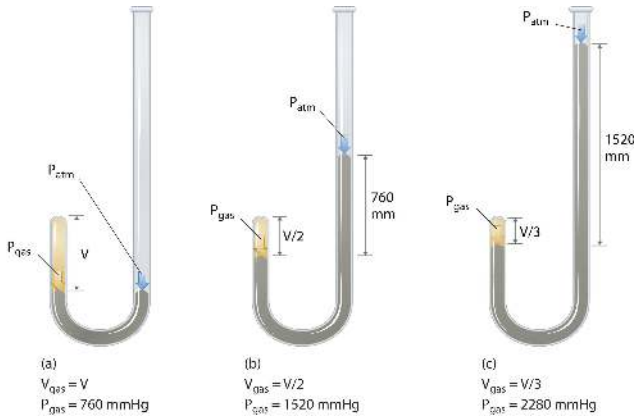


Figure 6.3.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is *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.

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{6.3.2}$$

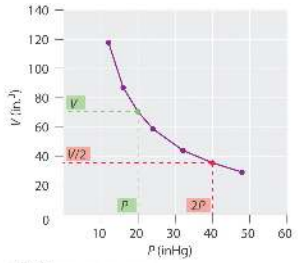
or

$$V \propto \frac{1}{P} \tag{6.3.3}$$

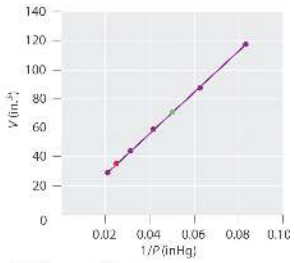
where the ∝ symbol is read “is proportional to.” A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equation 6.2.1 and Equation 6.2.3. Dividing both sides of Equation 6.2.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of 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 law, 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.*

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) Data from Boyle’s experiment



(b) Volume vs. pressure



(c) Volume vs. 1/pressure

Figure 6.3.2: Plots of Boyle’s Data. (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.



Boyle’s Law: https://youtu.be/lu86VSupPO4

The Relationship between Temperature and Volume: Charles's Law

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 6.3.3).A sample of 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. Note from part (a) in Figure 6.3.3 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at −273.15°C. Similarly, as shown in part (b) in Figure 6.3.3, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

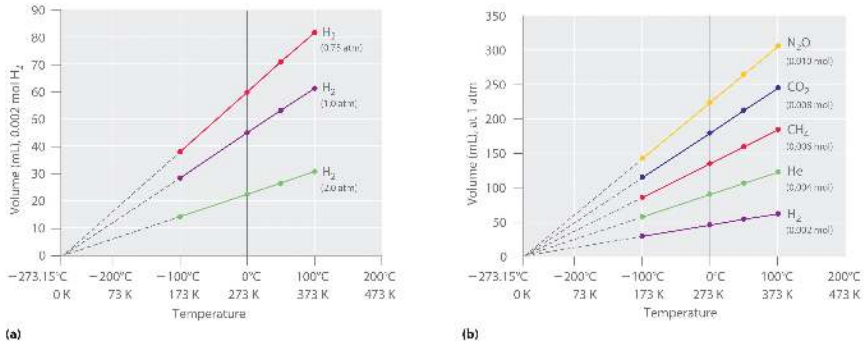


Figure 6.3.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. 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 significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

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 kelvins). This relationship, illustrated in part (b) in Figure 6.3.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const. } T \tag{6.3.4}$$

or

$$V \propto T \tag{6.3.5}$$

with *temperature expressed in kelvins*, not *in degrees Celsius.* Charles's law is valid for virtually all gases at temperatures well above their boiling points.



Charles's Law: https://youtu.be/NBf510ZnlR0

The Relationship between Amount and Volume: Avogadro's Law

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 (Figure 6.3.4). This is the historic "Avogadro's hypothesis."

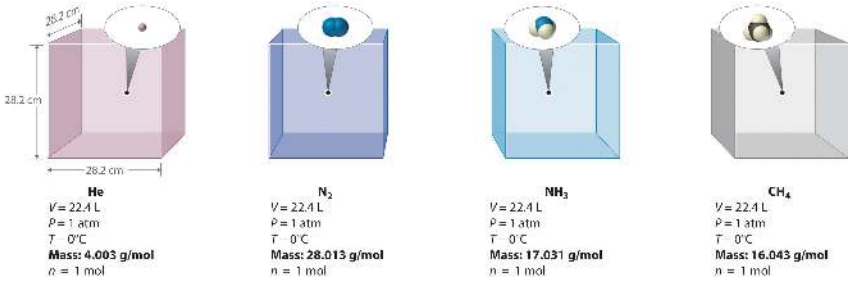


Figure 6.3.4: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas.

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) 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,

$$V = \text{const.}\ (n) \tag{6.3.6}$$

or

$$V \propto .\, n @ \text{ constant T and P} \tag{6.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

Note

For a sample of gas,

- V increases as P decreases (and vice versa)
- V increases as T increases (and vice versa)
- V increases as n increases (and vice versa)

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure 6.3.5. Volume *increases* with increasing temperature or amount but *decreases* with increasing pressure.

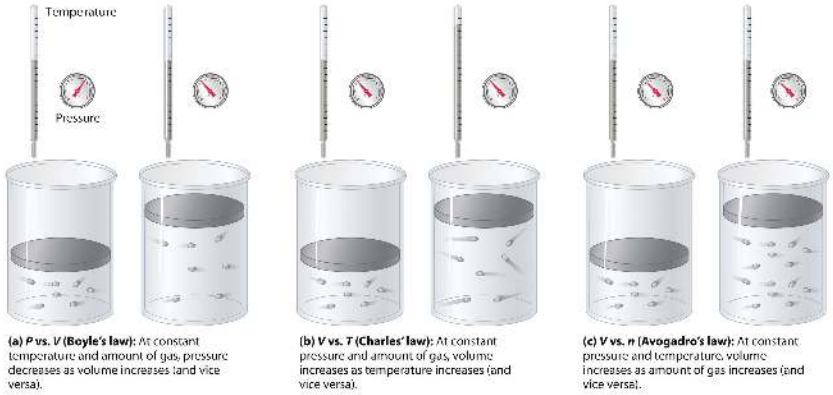


Figure 6.3.5: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts.



Avogadro's Law: https://youtu.be/dRY3Trl4T24

Summary

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. 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.

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- **6.2: The Simple Gas Laws** is licensed CC BY-NC-SA 4.0.

6.4 The Ideal Gas Law

Learning Objectives

- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between Pressure, Temperature, Volume, and Amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions are as follows:

- **Boyle's law**

$$V \propto \frac{1}{P} \quad @ \text{ constant n and T} \tag{1}$$

- **Charles's law**

$$V \propto T \quad @ \text{ constant n and P} \tag{2}$$

- **Avogadro's law**

$$V \propto n \quad @ \text{ constant T and P} \tag{3}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{6.3.1}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.} \left(\frac{nT}{P} \right) \tag{6.3.2}$$

By convention, the proportionality constant in Equation 6.3.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 6.3.2 gives

$$V = \frac{Rnt}{P} = \frac{nRT}{P} \tag{6.3.3}$$

Clearing the fractions by multiplying both sides of Equation 6.3.4 by P gives

$$PV = nRT \tag{6.3.4}$$

This equation is known as the **ideal gas law**.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. The ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

Note

Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.

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

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{6.3.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{6.3.6}$$

Standard Conditions of Temperature and Pressure

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 bar = 100 kPa = 10^5 Pa pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ bar} = 10^5 \text{ Pa} \tag{4}$$

Please note that STP was defined differently in the part. The old definition was based on a standard pressure of 1 atm.

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 6.3.4:

$$V = \frac{nRT}{P} \tag{6.3.7}$$

Thus the volume of 1 mol of an ideal gas is **22.71 L at STP** and **22.41 L at 0°C and 1 atm**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, 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 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table 1: Molar Volumes of Selected Gases at 0°C and 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 1

The balloon that Charles used for his initial flight 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 6.3.4) for *n*, we obtain

$$745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.980 \text{ atm} \tag{5}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K} \tag{6}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980 \text{ atm} \times 31150 \text{ L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303 \text{ K}} = 1.23 \times 10^3 \text{ mol} \tag{7}$$

? Exercise 1

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 1, 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 5.



The Ideal Gas Law: https://youtu.be/rHGs23368mE

General Gas Equation

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{array}{ll} \text{Initial condition } (i) & \text{Final condition} (f) \\ P_iV_i = n_iRT_i & P_fV_f = n_fRT_f \end{array} \tag{8}$$

Both equations can be rearranged to give:

$$R = \frac{P_iV_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f} \tag{9}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f} \tag{6.3.8}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.

Example 2

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 (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 1?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example 1 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to −10°C. Begin by constructing a table showing the initial and final conditions.
B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.
C. 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:

Initial (August)	Final (January)
T_i = 30°C = 303 K	T_f = −10°C = 263 K
P_i = 0.980 atm	P_f = 0.980 atm
n_i = 1.23 × 103 mol	n_f = 1.23 × 103 mol
V_i = 31150 L	V_f = ?

B Both n and P are the same in both cases ($n_i = n_f$, $P_i = P_f$). Therefore, Equation can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{10}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150 \text{ L} \times \frac{263 \text{ K}}{303 \text{ K}} = 2.70 \times 10^4 \text{ L} \tag{11}$$

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 2

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 1 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, 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 1 can be applied in *any* such case, as we demonstrate in Example 2 (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 3

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 5.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Initial	Final
$V_i = 0.406\ \text{L}$	$V_f = 0.406\ \text{L}$
$n_i = 0.025\ \text{mol}$	$n_f = 0.025\ \text{mol}$
$T_i = 25\ ^\circ\text{C} = 298\ \text{K}$	$T_i = 750\ ^\circ\text{C} = 1023\ \text{K}$
$P_i = 1.5\ \text{atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$P_i T_i = P_f T_f \tag{12}$$

By solving the equation for P_f, we get:

$$P_f = P_i \times \frac{T_i}{T_f} = 1.5\ \text{atm} \times \frac{1023\ \text{K}}{298\ \text{K}} = 5.1\ \text{atm} \tag{13}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

? Exercise 3

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

In Example 1 and Example 2, two of the four parameters (*P*, *V*, *T*, and *n*) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables *P*, *V*, and *T* are allowed to vary for a given sample of gas (hence *n* is constant), and we are interested in the change in the value of the third under the new conditions.

Example 4

We saw in Example 1 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 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 5.

Solution:

Begin by setting up a table of the two sets of conditions:

Initial	Final
$P_i = 745\ \text{mmHg} = 0.980\ \text{atm}$	$P_f = 312\ \text{mmHg} = 0.411\ \text{atm}$
$T_i = 30\ ^\circ\text{C} = 303\ \text{K}$	$T_f = 750 - 30\ ^\circ\text{C} = 243\ \text{K}$
$n_i = 1.2 \times 10^3\ \text{mol}$	$n_i = 1.2 \times 10^3\ \text{mol}$
$V_i = 31150\ \text{L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 6.3.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{14}$$

By solving the equation for V_f, we get:

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} = 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}} = 5.96 \times 10^4\ \text{L} \tag{15}$$

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:

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 4

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: 4.07×10^3



Second Type of Ideal Gas Law Problems: https://youtu.be/WQDJOqddPI0

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

$$\frac{n}{V} = \frac{P}{RT} \tag{6.3.9}$$

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):

$$n = \frac{m}{M} \tag{6.3.10}$$

Substituting this expression for n into Equation 6.3.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{6.3.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{6.3.12}$$

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 5

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 6.3.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol} \tag{16}$$

Using 0.08206 (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:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm} \tag{17}$$

B Substituting these values into Equation 6.3.12 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L} \tag{18}$$

? Exercise 5

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 6.3.12 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 reweighed. 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 6.

✔ Example 6

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 6.3.12 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 6.3.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{19}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L} \tag{20}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K \tag{21}$$

$$P = 727\text{mmHg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm} \tag{22}$$

The molar mass of the unknown gas is thus

$$\rho = \frac{1.84\text{ g/L} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol} \tag{23}$$

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:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol} \tag{24}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol} \tag{25}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol} \tag{26}$$

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 6

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



Density and the Molar Mass of Gases: https://youtu.be/gnkGBsvUFVk

Summary

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.

Ideal gas equation: $PV = nRT$,

where $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

General gas equation: $\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$

Density of a gas: $\rho = \frac{MP}{RT}$

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.

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- **6.3: Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation** is licensed CC BY-NC-SA 4.0.

6.5 Mixtures of Gases

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:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{1}$$

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 pressure, 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 pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{2}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

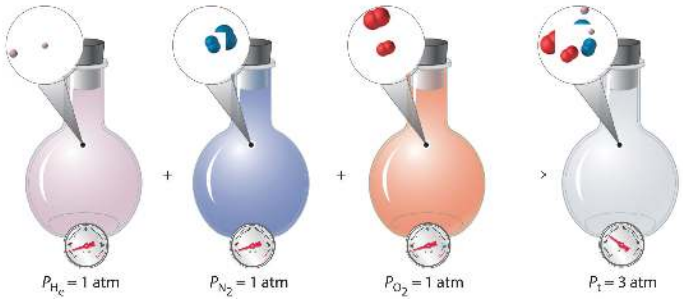


Figure 1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{3}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{4}$$

$$P_{tot} = \sum_{i=1}^{n} n_i \left(\frac{RT}{V} \right) \tag{5}$$

Equation 6.6.4 restates Equation 6.6.3 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 6.6.4 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 1.

Example 1

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

$$n_{\text{He}} = \frac{326.4 \text{ g}}{4.003 \text{ g/mol}} = 81.54 \text{ mol} \tag{6}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2 \text{ g}}{32.00 \text{ g/mol}} = 1.60 \text{ mol} \tag{7}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}} RT}{V} = \frac{81.54 \text{ mol} \times 0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}}{10.0 \text{ L}} = 196.2 \text{ atm} \tag{8}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2} RT}{V} = \frac{1.60 \text{ mol} \times 0.08206 \dfrac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}}{10.0 \text{ L}} = 3.85 \text{ atm} \tag{9}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85) \text{ atm} = 200.1 \text{ atm} \tag{10}$$

Exercise 1

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: $P_{CH_4} = 137\ atm$; $P_{C_2H_6} = 13.4\ atm$; $P_{tot} = 151\ atm$

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) 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_{tot}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{11}$$

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 $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{12}$$

Rearranging this equation gives

$$P_A = x_A P_{tot} \tag{13}$$

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. 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 6.6.7, 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 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_{tot}	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 6.6.7.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{14}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$x_{\mathrm{CO_2}} = \frac{48\ \mathrm{mmHg}}{767\ \mathrm{mmHg}} = 0.063 \tag{15}$$

The following table gives the values of x_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

? Exercise 2

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

$$P_{\mathrm{CO_2}} = 86\ \mathrm{atm},\ P_{\mathrm{N_2}} = 2.7\ \mathrm{atm}$$



Dalton's Law of Partial Pressures: https://youtu.be/y5-SbspyvBA

Summary

- The partial pressure of each gas in a mixture is proportional to its mole fraction.

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.

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6.6: Gas Volumes and Stoichiometry

Learning Objectives

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.
- To understand how 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.

Introduction

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 6.6.1

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:

$$2S_{(s)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)} \tag{6.6.1}$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) 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:

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 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4 \tag{6.6.2}$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3 \text{mol } O_2}{2 \text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2 \tag{6.6.3}$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L} \tag{6.6.4}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 ton of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

? Exercise 6.6.1

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:

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + FeCl_{2(aq)} \tag{6.6.5}$$

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)



Ideal Gas law Equation and Reaction Stoichiometry: https://youtu.be/8pPlW8MRhgI

Collecting gases over water

As shown in Figure 6.6.1, a common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of 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 ($P_{\text{bar.}}$).

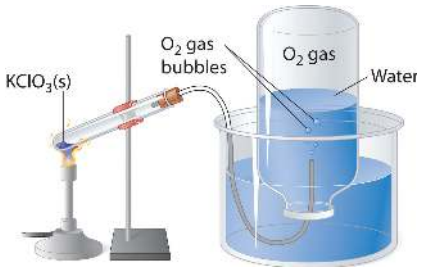


Figure 6.6.1: An Apparatus for Collecting Gases by the Displacement of Water

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. 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 6.6.1, 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:

$$P_{tot} = P_{gas} + P_{H_2O} = P_{bar.} \tag{6.6.6}$$

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 6.6.1).

Table 6.6.1: Vapor Pressure of Water at Various Temperatures

T (°C)	*P* (in mmHg)
0	4.58
15	12.79
17	14.53
19	16.48
21	18.65
23	21.07
25	23.76
30	31.82
50	92.51
70	233.8
100	760.0

As shown in Figure 6.6.2, 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 6.6.2. 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).

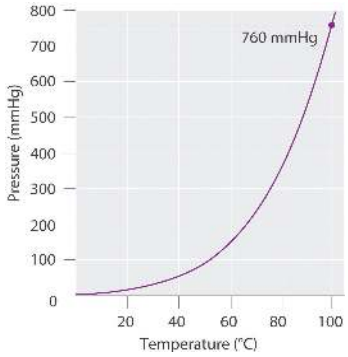


***Figure* 6.6.2:** *A Plot of the Vapor Pressure of Water versus Temperature. The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.*

Example 6.6.2

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na_{(s)} + 3N_{2\ (g)} \tag{6.6.7}$$

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 6.6.1, what volume of gas would be produced at 21°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 6.6.1, 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:

$$\frac{5.00\text{ g NaN}_3}{(22.99+3\times14.01)\text{ g/mol}}\times\frac{3\text{mol N}_2}{2\text{mol NaN}_3}=0.115\text{ mol N}_2 \tag{6.6.8}$$

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 6.6.1 tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the N_2 gas in the flask is only

$$(762-18.65)\text{ mmHg}\times\frac{1\text{ atm}}{760\text{ atm}}=743.4\text{ mmHg}\times\frac{1\text{ atm}}{760\text{ atm}}=0.978\text{ atm.} \tag{6.6.9}$$

B Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V=\frac{nRT}{P}=\frac{0.115\text{ mol}\times0.08206\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}\times294\text{ K}}{0.978\text{ atm}}=2.84\text{ L} \tag{6.6.10}$$

? Exercise 6.6.2

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



Collecting a Product Gas over Water: https://youtu.be/zFuy3t81vjQ

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.

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

- 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?
- 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?
- 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.
- 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: $C_{10}H_{10}O_3N_2$

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6.7: Kinetic Molecular 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 gases 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.

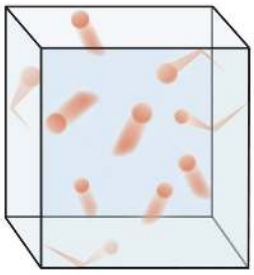


Figure 6.7.1 Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

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 gases we have been discussing. In Section 10.8, we explain how this theory must be modified to account for the behavior of real 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 6.7.2).

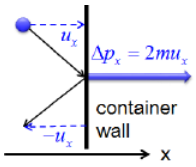


Figure 6.7.2 Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transfered to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule 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:

$$\Delta p_x = 2mu_x \tag{6.7.1}$$

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.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{6.7.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{6.7.3}$$

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 :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{6.7.4}$$

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:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{6.7.5}$$

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. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas ($\overline{e_K}$), which can be represented as *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{6.7.6}$$

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:

$$N_A\overline{e_K} = \frac{1}{2} M\overline{u^2} = \frac{3}{2}RT \tag{6.7.7}$$

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_{rms}) and the temperature.

The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{6.7.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{6.7.9}$$

In this equation, u_{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_{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 6.7.8 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

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

Example 6.7.1

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_{av}) root mean square speed (v_{rms}), and most probable speed (v_{m}).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_{m})

Strategy:

Use Equation 6.7.6 to calculate the average speed and Equation 6.7.8 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:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s} \tag{6.7.10}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s} \tag{6.7.11}$$

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 $v_{\text{m}} = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

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 6.7.1. 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 6.7.1 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

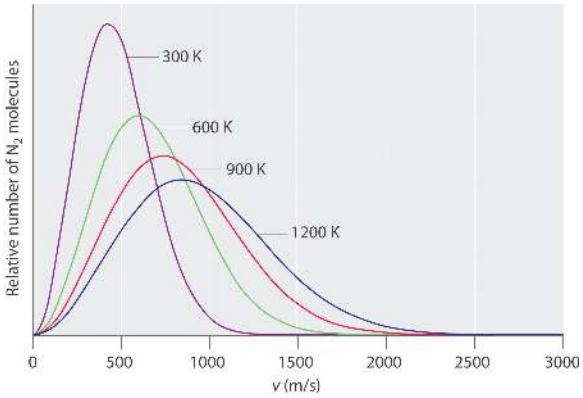


Figure 6.7.2 The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

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 6.7.2

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 6.7.2

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



Kinetic-Molecular Theory of Gases: https://youtu.be/9f83XAYfXAg

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{6.7.12}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{6.7.13}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{6.7.14}$$

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.

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6.8: Connecting Gas Properties to Kinetic Molecular Theory

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant and random 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.

Diffusion 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. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, effusion, 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 *is referred to as Graham's law*, 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*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{6.8.1}$$



Ethylene oxide

Figure 6.8.1 for 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. Hence, mylar balloons can retain their helium for days.

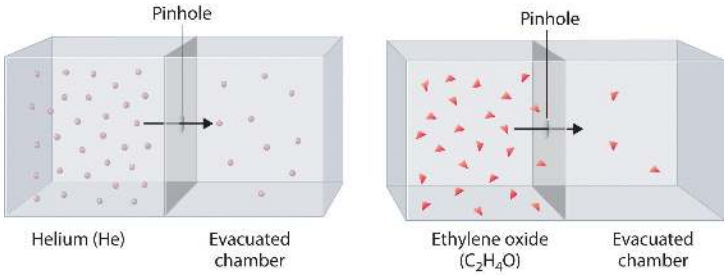


Figure 6.8.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

Note

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 6.8.1

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 nth 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. The molar mass of $^{238}UF_6$ is 238.05 + (6)(18.998) = 352.04 g/mol

   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 6.8.1:

$$\frac{\text{rate } ^{235}UF_6}{\text{rate } ^{238}UF_6} = \sqrt{\frac{352.04\ \text{g/mol}}{349.03\ \text{g/mol}}} = 1.0043 \tag{6.8.2}$$

2.

   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% $^{235}UF_6$.

3. **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: final purity = (initial purity)(separation)^n

   In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$1.0043^n = \frac{0.990}{0.00720} = 137.50 \tag{6.8.3}$$

4. Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{6.8.4}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} = 1148 \tag{6.8.5}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Figure 6.8.2 shows a small part of a system that is used to prepare enriched uranium on a large scale.



Figure 6.8.2: 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.

? Exercise 6.8.1

Helium consists of two isotopes: ^{3}He (natural abundance = 0.000134%) and ^{4}He (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 ^{4}He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^{3}He and ^{4}He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^{3}He?

Answer: a. ratio of effusion rates = 1.15200; one step gives 0.000154% ^{3}He; b. 96 steps

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:

$$KE = \frac{1}{2}\frac{M_\text{A}}{N_A} v_{\text{rms,A}}^2 = \frac{1}{2}\frac{M_\text{B}}{N_A} v_{\text{rms,B}}^2 \tag{6.8.6}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{\text{rms,B}}^2}{v_{\text{rms,A}}^2} = \frac{M_\text{A}}{M_\text{B}} \tag{6.8.7}$$

Taking the square root of both sides gives

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_\text{A}}{M_\text{B}}} \tag{6.8.8}$$

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 6.8.4 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 6.8.3 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.

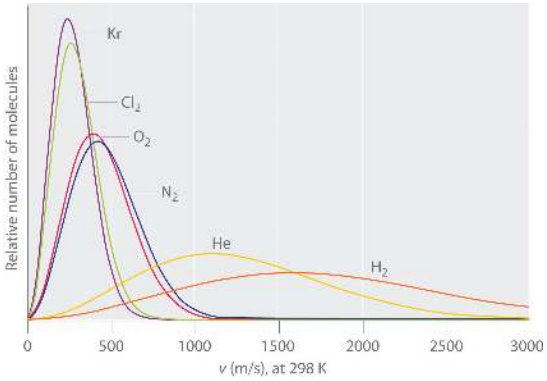


Figure 6.8.3: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

Note

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 6.8.4.

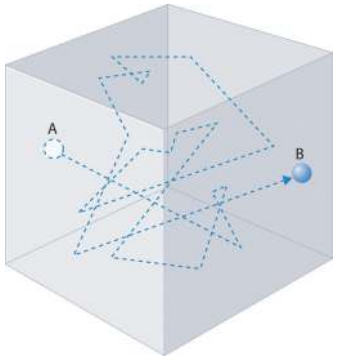


Figure 6.8.4: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

The average distance traveled by a molecule between collisions is the mean free path. 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 6.0×10^{-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 1×10^{10} m (about 6 million miles).

Note

The **denser** the gas, the **shorter** the mean free path.

Example 6.8.2

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 6.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 6.8.4, 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

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3145 \ \dfrac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} = 361 \ \text{m/s} \tag{6.8.9}$$

or approximately 810 mi/h.

Exercise 6.8.2

Calculate the rms speed of a sample of radon gas at 23°C.

Answer: 1.82×10^2 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 Section 10.8, we explore how the behavior of real gases differs from that of ideal gases.



Graham’s law of Diffusion and Effusion: https://youtu.be/9HO-qgh-iGI

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{6.8.10}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{6.8.11}$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{6.8.12}$$

- **Graham's law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{6.8.13}$$

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.

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6.9: Chapter Problems

Application Problems

Be sure you are familiar with the material in Essential Skills 5 (Section 10.9 "Essential Skills 5") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. ♦ Oxalic acid ($C_2H_2O_4$) is a metabolic product of many molds. Although oxalic acid is toxic to humans if ingested, many plants and vegetables contain significant amounts of oxalic acid or oxalate salts. In solution, oxalic acid can be oxidized by air via the following chemical equation:

   $H_2C_2O_4(aq) + O_2(g) \rightarrow H_2O_2(l) + 2\ CO_2(g)$

   If a plant metabolized enough oxalic acid to produce 3.2 L of CO_2 on a day when the temperature was 29°C and the pressure was 752 mmHg, how many grams of oxalic acid were converted to CO_2? Given that air is 21% oxygen, what volume of air was needed for the oxidation?

2. ♦ The decomposition of iron oxide is used to produce gas during the manufacture of porous, expanded materials. These materials have very low densities due to the swelling that occurs during the initial rapid heating. Consequently, they are used as additives to provide insulation in concrete, road building, and other construction materials. Iron oxide decomposes at 1150°C according to the following chemical equation:

   $6\ Fe_2O_3(s) \rightarrow 4\ Fe_3O_4(s) + O_2(g)$

   1. Explain how this reaction could cause materials containing Fe_2O_3 to swell on heating.
   2. If you begin with 15.4 g of Fe_2O_3, what volume of O_2 gas at STP is produced?
   3. What is the volume of the same amount of O_2 gas at 1200°C, assuming a constant pressure of 1.0 atm?
   4. If 6.3 L of gas were produced at 1200°C and 1 atm, how many kilograms of Fe_2O_3 were initially used in the reaction? How many kilograms of Fe_3O_4 are produced?

3. ♦ A 70 kg man expends 480 kcal of energy per hour shoveling snow. The oxidation of organic nutrients such as glucose during metabolism liberates approximately 3.36 kcal of energy per gram of oxygen consumed. If air is 21% oxygen, what volume of air at STP is needed to produce enough energy for the man to clear snow from a walkway that requires 35 minutes of shoveling?

4. ♦ Calcium carbonate is an important filler in the processing industry. Its many uses include a reinforcing agent for rubber and improving the whiteness and hiding power of paints. When calcium nitrate is used as a starting material in the manufacture of fertilizers, calcium carbonate is produced according to the following chemical reaction:

   $Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ NH_4NO_3$

   1. What volume of CO_2 at STP is needed to react completely with 28.0 g of calcium nitrate?
   2. What volume of ammonia at STP is needed to react with the amount of calcium nitrate?
   3. If this reaction were carried out in Denver, Colorado (pressure = 630 mmHg), what volumes of CO_2 and NH_3 at room temperature (20°C) would be needed?

5. ♦ Calcium nitrate used in the process described in Problem 4 is produced by the reaction of fluoroapatite—$Ca_5[(PO_4)_3(F)]$—with nitric acid:

   $Ca_5[(PO_4)_3(F)] + 10\ HNO_3 \rightarrow 5\ Ca(NO_3)_2 + HF + 3\ H_3PO_4\ Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ NH_4NO_3$

   1. Your lab is in Denver, Colorado, and you have a cylinder with 8.40 L of CO_2 at room temperature (20°C) and 4.75 atm pressure. What would be the volume of the CO_2 gas at 630 mmHg? How many grams of fluoroapatite could be converted to $CaCO_3$ using the two reactions and this amount of CO_2?
   2. If 3.50 L of a 0.753 M HF solution was produced during the conversion of fluoroapatite to calcium nitrate, how many grams of calcium carbonate could you produce, assuming 100% efficiency?
   3. How many liters of ammonia gas at this higher altitude and 20°C are required to convert the calcium nitrate to calcium carbonate *and* to neutralize all of the HF solution?
   4. If the reaction of fluoroapatite with nitric acid takes place at 330 atm and 80°C, what volumes of NH_3 and CO_2 are needed to convert 20.5 kg of fluoroapatite to calcium carbonate?

6. Mars has an average temperature of −47°C; a surface pressure of 500 Pa; and an atmosphere that is 95% carbon dioxide, 3% nitrogen, and 2% argon by mass, with traces of other gases. What is the partial pressure (in atmospheres) of each gas in this atmosphere? A 5.0 L sample is returned to Earth and stored in a laboratory at 19°C and 1 atm. What is the volume of this sample?

7. ♦ Chlorofluorocarbons (CFCs) are inert substances that were long used as refrigerants. Because CFCs are inert, when they are released into the atmosphere they are not rapidly destroyed in the lower atmosphere. Instead, they are carried into the stratosphere, where they cause ozone depletion. A method for destroying CFC stockpiles passes the CFC through packed sodium oxalate ($Na_2C_2O_4$) powder at 270°C. The reaction for Freon-12 (CF_2Cl_2) is as follows:

   $CF_2Cl_2(g) + 2\ Na_2C_2O_4(s) \rightarrow 2\ NaF(s) + 2\ NaCl + C(s) + 4\ CO_2(g)$

   1. If this reaction produced 11.4 L of CO_2 gas at 21°C and 752 mmHg, what mass of sodium oxalate was consumed in the reaction?
   2. If you had to design a reactor to carry out the reaction at a maximum safe pressure of 10.0 atm while destroying 1.0 kg of Freon-12, what volume reactor would you need?
   3. A 2.50 L reaction vessel is charged with 20.0 atm of Freon-12 and excess sodium oxalate at 20°C. The temperature is increased to 270°C, and the pressure is monitored as the reaction progresses. What is the initial pressure at 270°C? What is the final pressure when the reaction has gone to completion?

8. ♦ The exhaust from a typical six-cylinder car contains the following average compositions of CO and CO_2 under different conditions (data reported as percent by volume; rpm = rotations per minute):

Species	Idling (1000 rpm)	Accelerating (4000 rpm)	Decelerating (800 rpm)
CO	1.0	1.2	0.60
CO_2	0.80	0.40	0.40

   1. What are the mole fractions of CO and CO_2 under each set of conditions?
   2. If the engine takes in 4.70 L of air at STP mixed with fine droplets of gasoline (C_8H_{18}) with each rotation, how many grams of gasoline are burned per minute?

9. Automobile airbags inflate by the decomposition of sodium azide (NaN_3), which produces sodium metal and nitrogen gas according to the following chemical equation:

   $2\ NaN_3 \rightarrow 2\ Na(s) + 3\ N_2(g)$

   How many grams of sodium azide are needed to inflate a 15.0 L airbag at 20°C and 760 mmHg? The density of NaN_3 is 1.847 g/cm^3. What is the volume of the gas produced compared to the solid reactant? Suggest a plausible reason to explain why skin burns can result from the inflation of an airbag during an automobile accident.

10. Under basic conditions, the reaction of hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$) produces oxygen and manganese dioxide. During a laboratory exercise, you carefully weighed out your sample of $KMnO_4$. Unfortunately, however, you lost your data just before mixing the $KMnO_4$ with an H_2O_2 solution of unknown concentration. Devise a method to determine the mass of your sample of $KMnO_4$ using excess H_2O_2.

11. Carbonated beverages are pressurized with CO_2. In an attempt to produce another bubbly soda beverage, an intrepid chemist attempted to use three other gases: He, N_2, and Xe. Rank the four beverages in order of how fast the drink would go “flat” and explain your reasoning. Which beverage would have the shortest shelf life (i.e., how long will an *unopened* bottle still be good)? Explain your answer.

12. ♦ Urea is synthesized industrially by the reaction of ammonia and carbon dioxide to produce ammonium carbamate, followed by dehydration of ammonium carbamate to give urea and water. This process is shown in the following set of chemical equations:

    $2\ NH_3(g) + CO_2(g) \rightarrow NH_2CO_2NH_4(s)\ NH_2CO_2NH_4(s) \rightarrow NH_2CONH_2(s) + H_2O(g)$

    1. A 50.0 L reaction vessel is charged with 2.5 atm of ammonia and 2.5 atm of CO_2 at 50°C, and the vessel is then heated to 150°C. What is the pressure in the vessel when the reaction has gone to completion? If the vessel is then cooled to 20°C, what is the pressure?

2. An aqueous solution of urea and water is drained from the reaction vessel. What is the molarity of the urea solution? Industrially, this reaction is actually carried out at pressures ranging from 130 to 260 atm and temperatures of approximately 180°C. Give a plausible reason for using these extreme conditions.

13. Explain what happens to the temperature, the volume, or the pressure of a gas during each operation and give the direction of heat flow, if any.

    1. The gas is allowed to expand from V_1 to V_2; a heat transfer occurs to maintain a constant gas temperature.
    2. The gas is allowed to expand from V_2 to V_3 with no concomitant heat transfer.
    3. The gas is compressed from V_3 to V_4; a heat transfer occurs to maintain a constant gas temperature.
    4. The gas is compressed from V_4 to V_1; no heat transfer occurs.

    These four processes constitute the cycle used in refrigeration, in which a gas such as Freon is alternately compressed and allowed to expand in the piston of a compressor. Which step eventually causes the food in a refrigerator to cool? Where does the thermal energy go that was removed in the cooling process?

Answers

1. 5.9 g oxalic acid, 7.8 L
2.
3. 278 L

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CHAPTER OVERVIEW

7: Electrons in Atoms

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In this chapter, we describe how electrons are arranged in atoms and how the spatial arrangements of electrons are related to their energies. We also explain how knowing the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element. As you study the material presented in this chapter, you will discover how the shape of the periodic table reflects the electronic arrangements of elements. In this and subsequent chapters, we build on this information to explain why certain chemical changes occur and others do not. After reading this chapter, you will know enough about the theory of the electronic structure of atoms to explain what causes the characteristic colors of neon signs, how laser beams are created, and why gemstones and fireworks have such brilliant colors. In later chapters, we will develop the concepts introduced here to explain why the only compound formed by sodium and chlorine is NaCl, an ionic compound, whereas neon and argon do not form any stable compounds, and why carbon and hydrogen combine to form an almost endless array of covalent compounds, such as CH_4, C_2H_2, C_2H_4, and C_2H_6. You will discover that knowing how to use the periodic table is the single most important skill you can acquire to understand the incredible chemical diversity of the elements.

Topic hierarchy

7.1: Electromagnetic Radiation
7.2: Atomic Spectra
7.3: Quantum Theory
7.4: The Bohr Atom
7.5: Leading to New Quantum Mechanics
7.6: Wave Mechanics
7.9: Electron Spin (A Fourth Quantum Number)

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7.1: Electromagnetic Radiation

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves among the types of electromagnetic waves.

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 7.1.1: 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 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 7.1.1). 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.

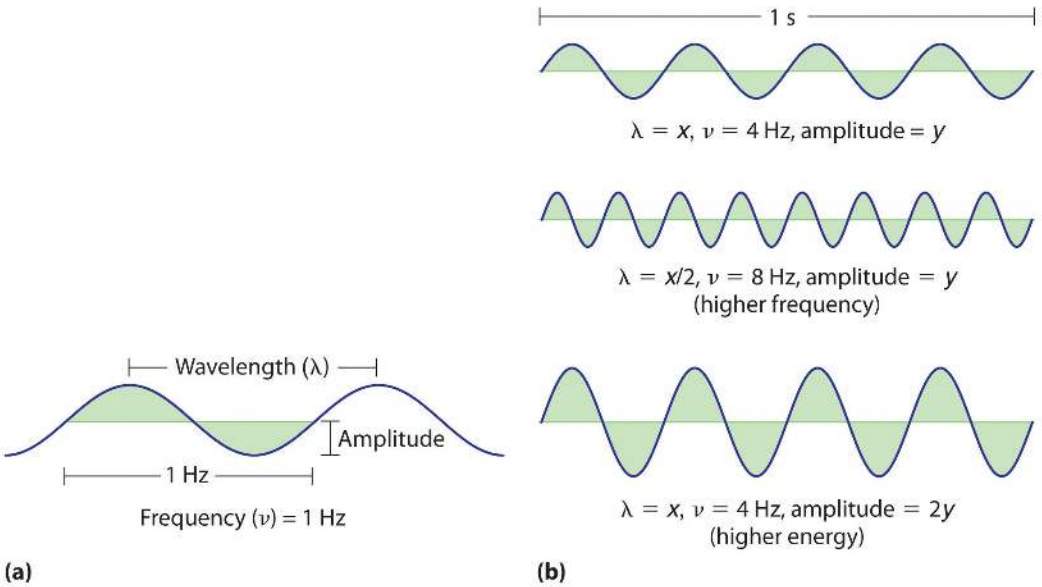


Figure 7.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 7.1.2). As you may have noticed in Figure 7.1.1, waves are periodic, 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), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. λ is the lowercase Greek lambda, and u 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 persecond (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 amplitude (the 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 7.1.2, 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 (ν), 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:

$$(\text{wavelength})(\text{frequency}) = speed \tag{7.1.1}$$

$$\lambda u = v \tag{7.1.2}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{second}\right) = \frac{meters}{second} \tag{7.1.3}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, u. 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.

Electromagnetic Radiation

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, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 7.1.3). Some forms of electromagnetic radiation are shown in Figure 7.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is 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.

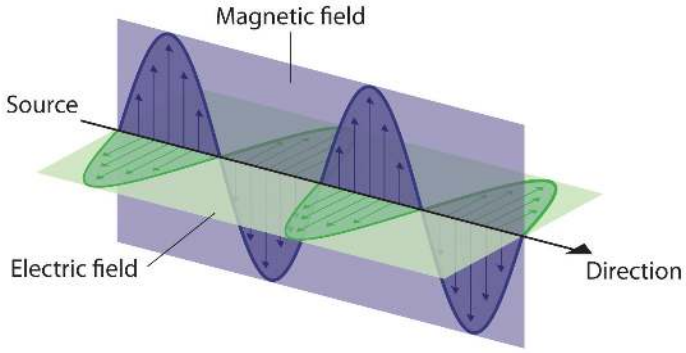


Figure 7.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure 7.1.4 and Table 7.1.1, 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 7.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$\begin{aligned} c &= \lambda u \\ u &= \frac{c}{\lambda} \end{aligned} \tag{7.1.4}$$

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, the wavelength increases.

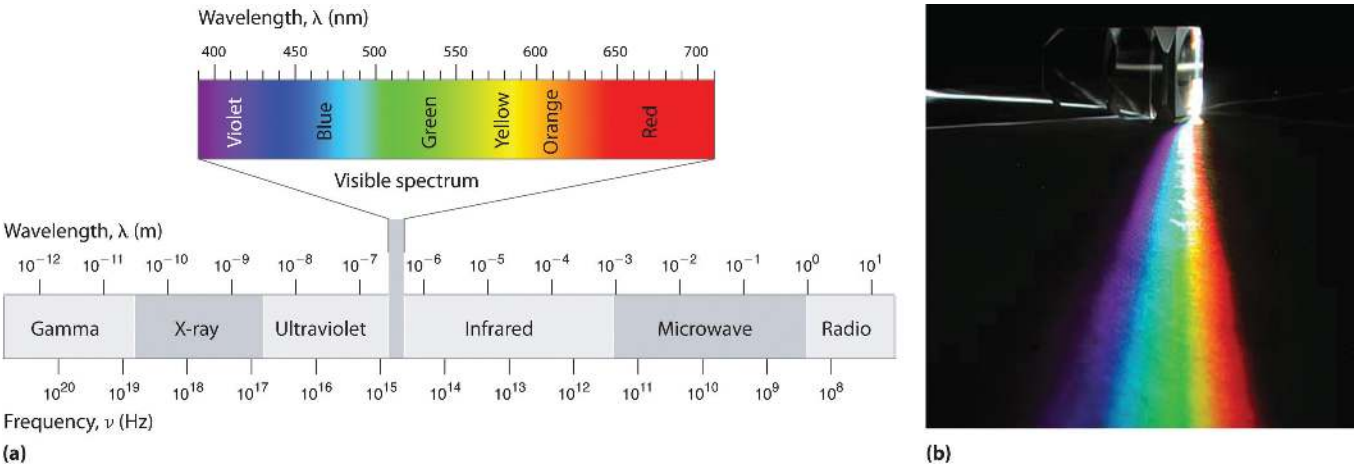


Figure 7.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum. (CC BY-NC-SA; anonymous)

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 7.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 7.1.1: 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:

$$E \propto u \tag{7.1.5}$$

$$E \propto \frac{1}{\lambda} \tag{7.1.6}$$

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 absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

The energy of electromagnetic radiation **increases** with **increasing** frequency and **decreasing** wavelength.

Example 7.1.1

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 7.1.2 to calculate the wavelength in meters.

Solution:

From Equation 7.1.4, 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:

$$\lambda\nu = c = 2.998 \times 10^8 m/s \tag{7.1.7}$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{u} = \left(\frac{2.988 \times 10^8 \ m/\cancel{s}}{101.1 \ \cancel{MHz}}\right)\left(\frac{1 \ \cancel{MHz}}{10^6 \ \cancel{s^{-1}}}\right) = 2.965 \ m \tag{7.1.8}$$

Exercise 7.1.1

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



Electromagnetic Radiation: https://youtu.be/TZy7a69pP-w

Summary

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. 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 in their frequencies and wavelengths.

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7.2: Atomic Spectra

Learning Objectives

- To know 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, 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, which is a spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths (Figure 7.2.1), 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 7.2.1: 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 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:

$$u = constant \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \tag{7.2.1}$$

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*:

$$\frac{1}{\lambda} = \Re \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{7.2.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of 1.09737 × 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.



Balmer 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,…). 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,…) 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.



The Bohr Atom: https://youtu.be/GuFQEOzFOgA

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. 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.

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.

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7.3: Quantum Theory

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, which is electromagnetic radiation whose wavelength and color that depends on the temperature of the object. 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 7.3.1: 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 a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

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 7.3.2. 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 7.3.2. 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

7.3.2, 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..

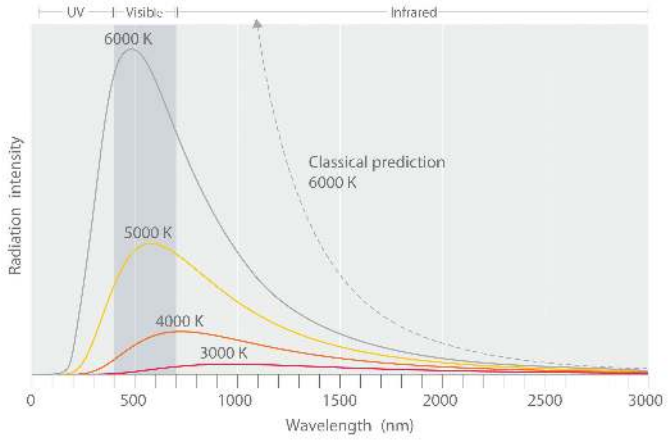
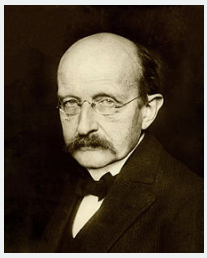


Figure 7.3.2: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 7.3.1 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 7.3.1). 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 Max Planck (1858–1947) by the equation

$$E = hu \tag{7.3.1}$$

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:

$$h = 6.626 \times 10^{-34}\ \text{J•s (joule-seconds)}$$

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 $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 7.3.2. 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 7.3.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

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.

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 7.3.3). 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).

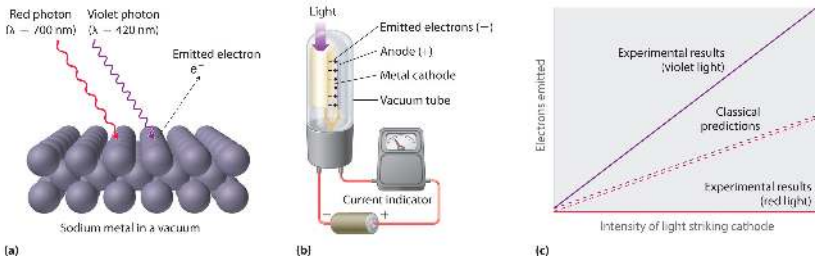


Figure 7.3.3: The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons 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 (a quantum of radiant energy, each of which possesses a particular energy energy E given by Equation 8.3.1 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:

$$kinetic\ energy\ of\ ejected\ electron = E - E_o = hu - hu_o = h\,(u - u_o) \tag{7.3.2}$$

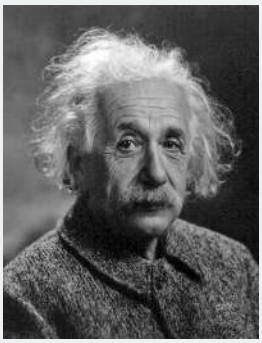
When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *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.



Figure 7.3.4: 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.

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 7.3.1

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure 7.3.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 6.1.2 and Equation 8.3.1 to calculate the energy in joules.

Solution:

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

Exercise 7.3.1

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

a. What is the energy in joules of a single photon?
b. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer

a. $1.287 \times 10^{-15}\ J/photon$

b. 4497 times



The Photoelectric Effect: https://youtu.be/mxBMxJLauQk

Summary

- The fundamental building blocks of energy are quanta and of matter are atoms.

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.

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7.4: The Bohr Atom

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

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*. 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*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\Re hc}{n^2} \tag{7.4.1}$$

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.

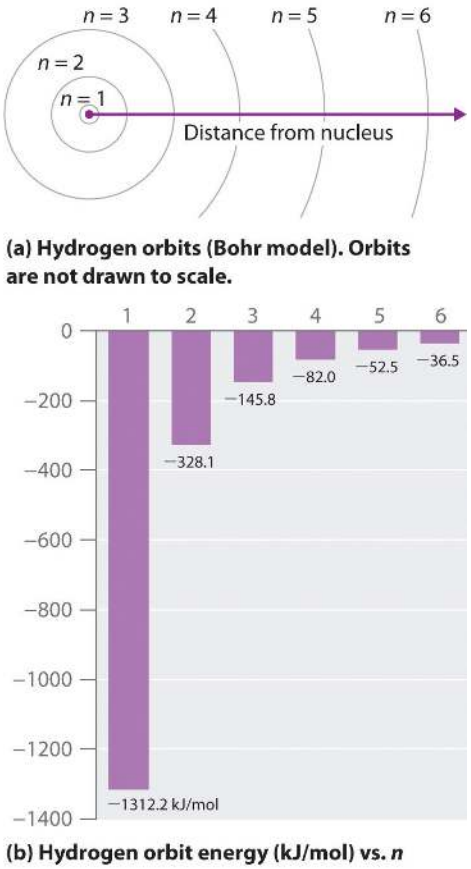
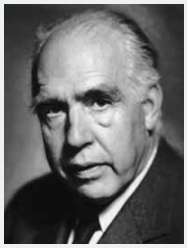


Figure 7.4.2 The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.

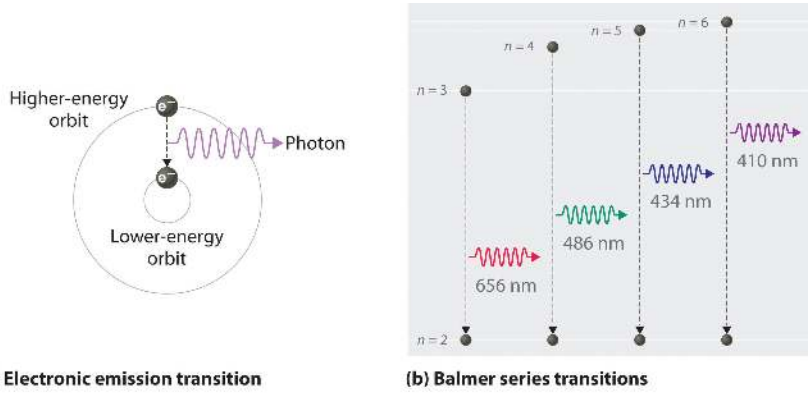
Niels Bohr (1885–1962)

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.

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 7.4.3 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 7.4.1).



(a) Electronic emission transition (b) Balmer series transitions

Figure 7.4.3: 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 $n \geq 3$ 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 (ΔE) 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 7.4.3) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{7.4.2}$$

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 7.4.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{7.4.3}$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{7.4.4}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation 7.4.5 and Equation 7.4.6 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 $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of 1.0974×10^7 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 7.4.3, 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 7.4.3). 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 ≥ 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 7.4.1). 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 ≥ 3. These transitions are shown schematically in Figure 7.4.4

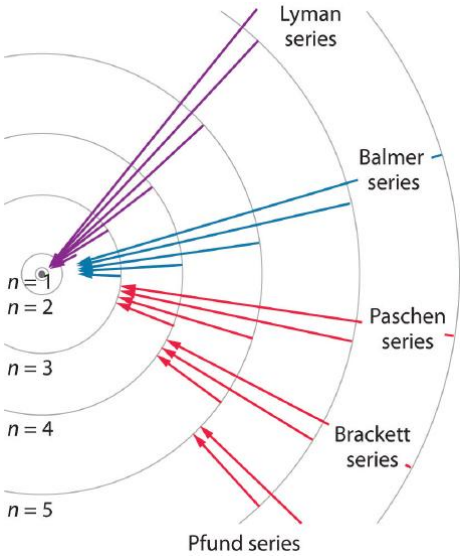


Figure 7.4.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to 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 7.4.1: The Lyman Series

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 7.4.2 (the Rydberg equation) and solve for λ.
B. Use Figure 7.4.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{7.4.5}$$

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.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1} \tag{7.4.6}$$

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=hu.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 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}.

$$\varpi = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m^{-1}}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1} \tag{7.4.7}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{7.4.8}$$

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 7.4.1: The Pfund Series

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 × 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 7.4.5). 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.

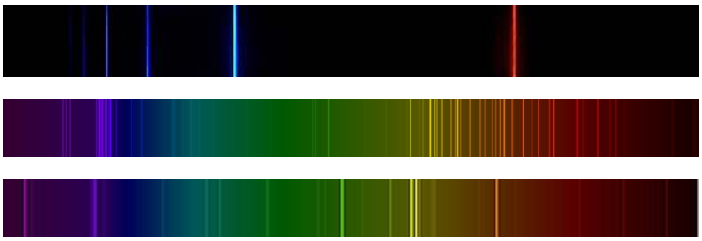


Figure 7.4.5: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The 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 spectrum (a 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 spectrum (a 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.

> 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.

The Energy States of the Hydrogen Atom

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.

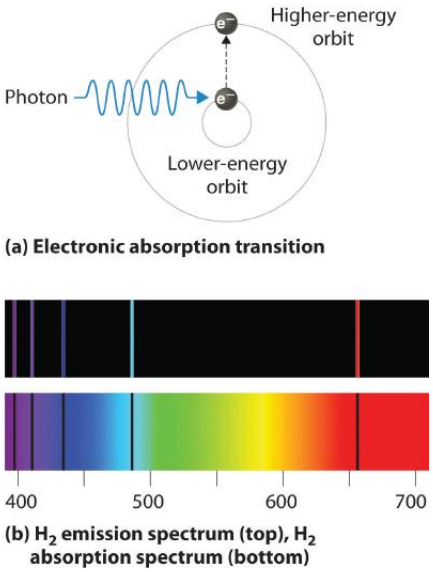


Figure 7.4.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

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 7.4.7 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.

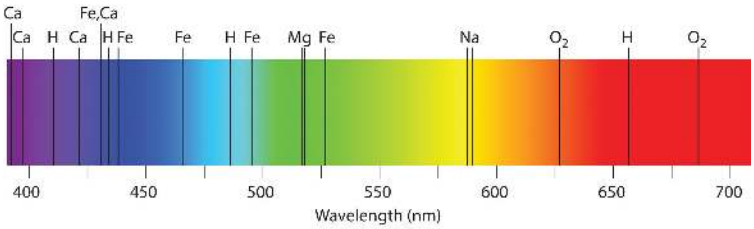


Figure 7.4.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption 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 7.4.5. 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 7.4.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

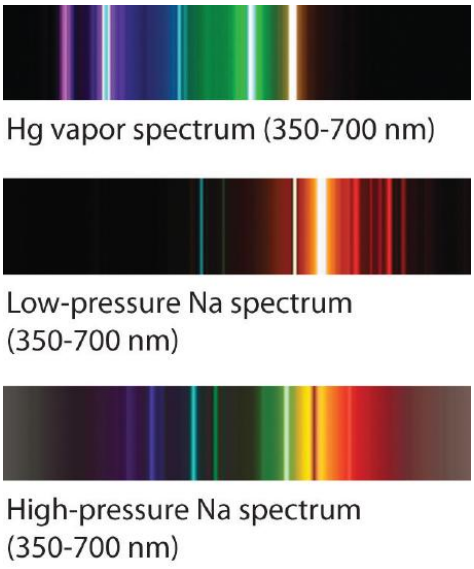


Figure 7.4.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. 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.



The Bohr Atom: https://youtu.be/GuFQEOzFOgA

The Chemistry of Fireworks

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure 7.4.9, 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.



Figure 7.4.9 :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.*

When oxidant/reductant mixtures listed in Table 7.4.1 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 7.4.9 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 7.4.1. 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.

Table 7.4.1: 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.



Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. 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.

Contributors and Attributions

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7.5: Leading to New Quantum Mechanics

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:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{7.5.1}$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{7.5.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a 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

$$\lambda = \frac{h}{mv} \tag{7.5.3}$$

where

- 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 7.5.1, Planck's constant (6.63×10^{-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 7.5.1

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 8.5.3 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

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot\ s^{-1}\right)} = 9.95 \times 10^{-35}\ m \tag{7.5.4}$$

(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 7.5.1

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 7.5.1, 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 7.5.1).

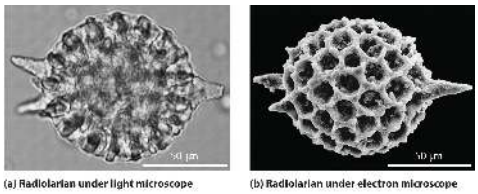


Figure 7.5.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope**.** Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (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 7.5.2a, on the right shows an arbitrary phase difference between two wave. Figure 7.5.2b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 7.5.2c 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.

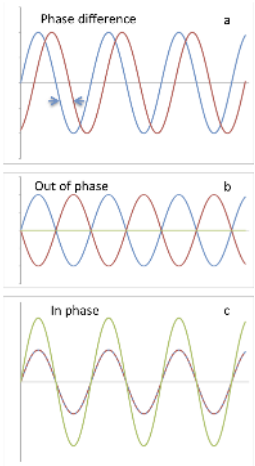


Figure 7.5.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase difference is 180 they completely cancel each other out.

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 wave (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 7.5.3). If the length of the string is *L*, then the lowest-energy vibration (the fundamental (the lowest-energy standing wave) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L \tag{7.5.5}$$

Higher-energy vibrations are called overtones (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n} \tag{7.5.6}$$

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 7.5.3 that all overtones have one or more nodes (the points 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.

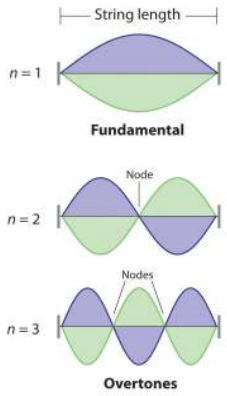


Figure 7.5.3 Standing Waves on a Vibrating String. The vibration with *n* = 1 is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain *n* − 1 nodes.

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

$$2\pi r = n\lambda \tag{7.5.7}$$

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 7.5.4). 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 8.5.2, 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.

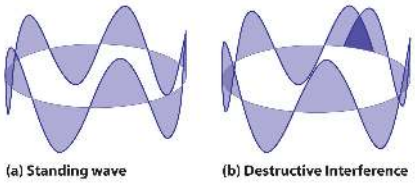


Figure 7.5.4 Standing Circular Wave and Destructive Interference.(a) In a standing circular wave with $n = 5$, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference 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.

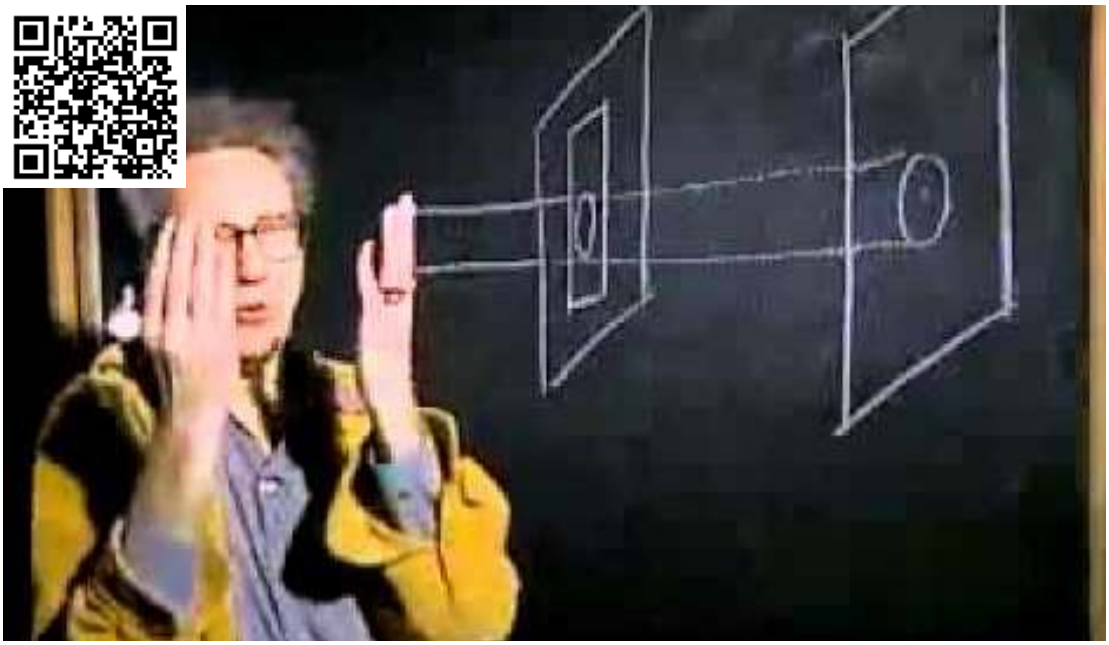


The de Broglie Equation: https://youtu.be/pz0zMHWtK7Q

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 electrons 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 principle is greater than or equal to Planck's constant h divided by 4π: states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{7.5.8}$$

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 ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{7.5.9}$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 8.5.8, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron ($1/2\ mv^2$) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ and we have no idea where the electron is.

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 7.5.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 7.5.1 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 8.5.7) to solve for the minimum uncertainty in the position of an object (Δx).
B. Find Δv 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 Δx.

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

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34}\ m$$

This is equal to 3.12×10^{-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 7.5.2

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: 6×10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Videos and Examples

- 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
- 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.

Summary

- An electron possesses both particle and wave properties.

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.

$$\lambda = \frac{h}{mv} \tag{8.5.3}$$

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.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{8.5.7}$$

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7.6: Wave Mechanics

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 developed the theory of quantum mechanics, which is used today to describe the energies and spatial distributions of electrons in atoms and molecules.

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.

Wave Functions

A wave function (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wave function is associated with a particular energy E. The properties of wave functions derived from quantum mechanics are summarized here:

- **A wave function uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z), and one specifies the time at which the object is at the specified location. For example, if you wanted to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 7.6.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

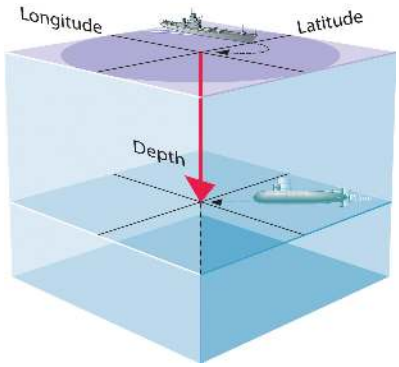


Figure 7.6.1: The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object

If you are the captain of a ship trying to intercept an enemy submarine, you need to deliver your depth charge to the right location at the right time.

- **The magnitude of the wave function at a particular point in space is proportional to the amplitude of the wave at that point.** Many wave functions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$,

represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wave function (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wave function should *not* be confused with a positive or negative electrical charge.

- **The square of the wave function at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wave function (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] is proportional to the probability of finding an electron at a given point. More accurately, the probability 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 $-i$. 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 distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 7.6.2.

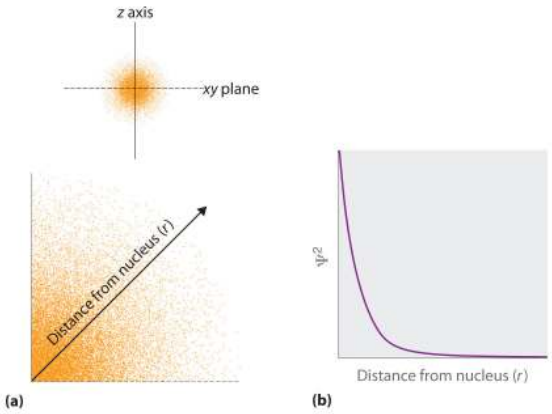


Figure 7.6.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus *r* for the ground state of the hydrogen atom, the electron probability density is greatest at *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.

- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wave function.** From the patterns of one- and two-dimensional standing waves shown in Figure 6.18 and Figure 6.19, you might expect (correctly) that the patterns of three-dimensional standing waves would be 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 flooded planet. Schrödinger incorporated Legendre's equations into his wave functions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wave functions), each of which is specified by a set of numbers called quantum numbers.
- **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 is a natural consequence of describing an electron as a standing wave.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (*n*, *l*, and m_l) to specify any wave function. The quantum numbers provide information about the spatial distribution of an electron. Although *n* can be any positive integer, only certain values of *l* and m_l are allowed for a given value of *n*.



Introduction to Quantum Numbers: https://youtu.be/07JpBeaPxL8

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{7.6.1}$$

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 shell 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*). 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:

$$l = 0, 1, 2, \ldots, n - 1 \tag{7.6.2}$$

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 subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.



Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell: https://youtu.be/ms7WR149fAY

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). 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:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{7.6.3}$$

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 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 7.6.1: n=4 Shell Structure

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:

Exercise 7.6.1: n=3 Shell Structure

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: *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 7.6.1):

- 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

Each principal shell has *n* subshells, and each subshell has $2l + 1$ orbitals.

Table 7.6.1 Values of n, l, and ml 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	



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): https://youtu.be/gbmGVUXBOBk

Summary

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

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**.

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7.9: Electron Spin (A Fourth Quantum Number)

Learning Objectives

- To introduce the concept of electron spin and demonstrated it is quantized

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.

The Stern-Gerlach Experiment

The quantum numbers n, l, m are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers n, l, m and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the figure 8.9.1. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

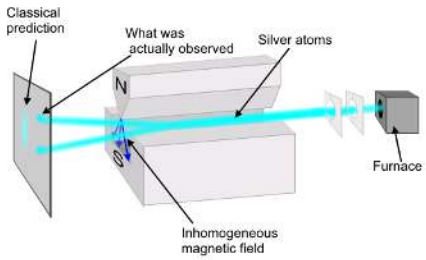


Figure 7.9.1: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* M arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to a *spin*, S; unlike position and momentum, which have clear classical analogs, spin does not.

The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Electron Spin

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. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

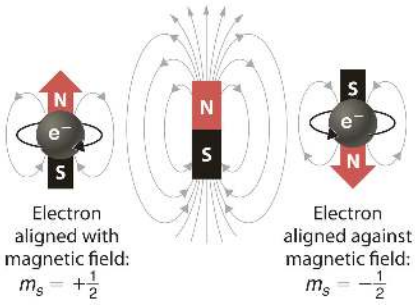


Figure 7.9.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 7.9.2). 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 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 principle: *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 was originally based on the physical and chemical properties of the known elements.

Example 7.9.2

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 $n = 2p$ 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 ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise 7.9.2

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

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).

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CHAPTER OVERVIEW

8: The Periodic Table

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The periodic table is a tabular arrangement of the chemical elements, ordered by their atomic number (number of protons in the nucleus), electron configurations, and recurring chemical properties. The periodic table can be used to derive relationships between the properties of the elements, and predict the properties of new elements yet to be discovered or synthesized. The periodic table provides a useful framework for analyzing chemical behavior, and is widely used in chemistry and other sciences.

Topic hierarchy

8.1: Classifying the Elements (Periodicity)
8.3: Sizes of Atoms and Ions
8.4: Ionization Energy
8.5: Electron Affinity
8.6: Magnetic Properties
8.7: Periodic Properties of the Elements

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8.1: Classifying the Elements (Periodicity)

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 triads (a set 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 8.1.1). (The noble gases were still unknown.) Newlands therefore suggested that the elements could be classified into octaves A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time)., corresponding to the *horizontal* rows in the main group elements. 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.

Note: John Newlands (1838–1898)

John Alexander Reina Newlands was an English chemist who worked on the development of the periodic table. He 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 8.1.1: 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 8.1.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density (ρ) 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):

$$\frac{molar\ mass\left(\not{g}/mol\right)}{density\left(\not{g}/cm^3\right)} = molar\ volume\ (cm^3/mol) \tag{8.1.1}$$

As shown in Figure 8.1.2, 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.

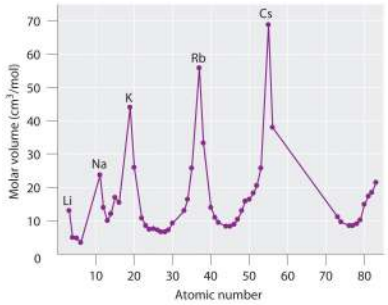
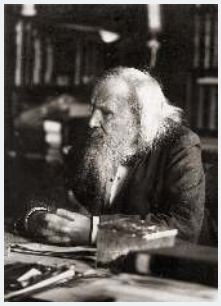


Figure 8.1.2: Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870. *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Note: 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.

Mendeleev's Periodic Table

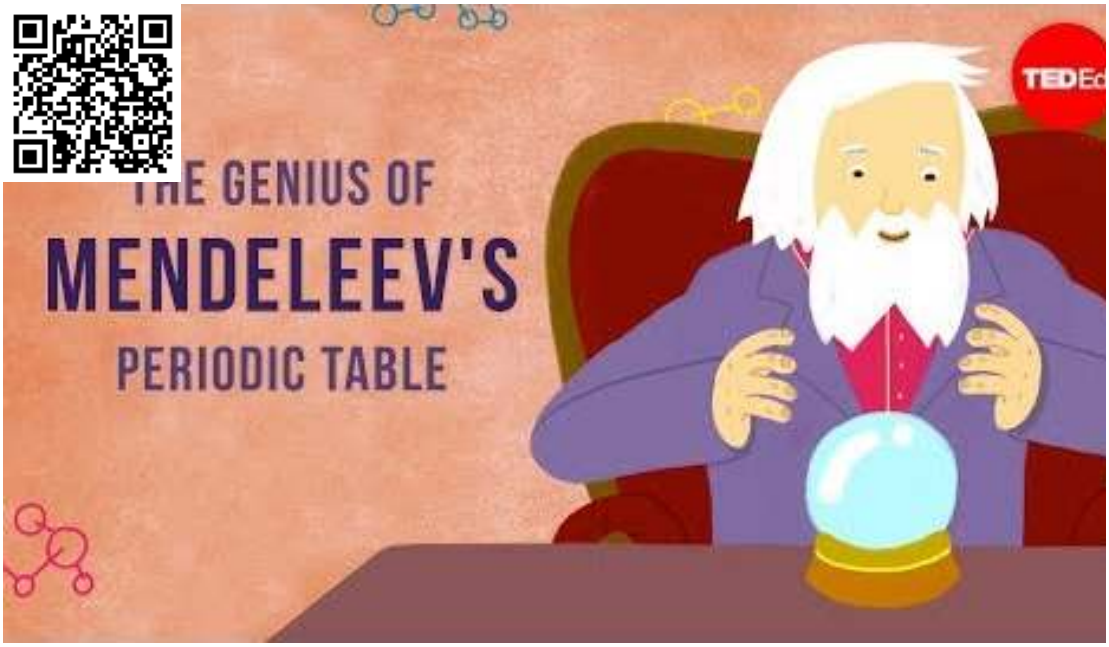
Mendeleev, who first published his periodic table in 1869 (Figure 8.1.3), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (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 8.1.3: 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 8.1.1). 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.



***Video* 8.1.1**: *The genius of Mendeleev's periodic table.*

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.

Table 8.1.1: 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
	ρ = 5.9 g/cm^3	ρ = 5.91 g/cm^3	ρ = 5.5 g/cm^3	ρ = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	ρ = 5.5 g/cm^3	ρ = 6.0 g/cm^3	ρ = 4.7 g/cm^3	ρ = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C

*mp = melting point; bp = boiling point.

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.

Note: 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 8.1.1

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 8.1.1

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 elements in the periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.

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.

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8.3: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

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 8.3.1 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.

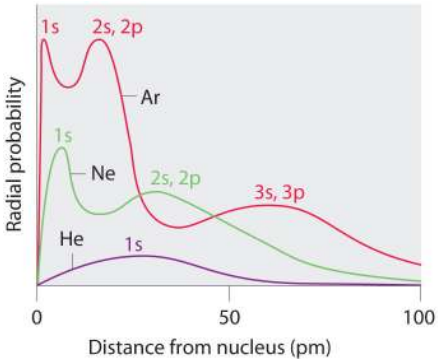


Figure 8.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure 8.3.1 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 8.3.1 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 8.3.2). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 \text{ Å} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.

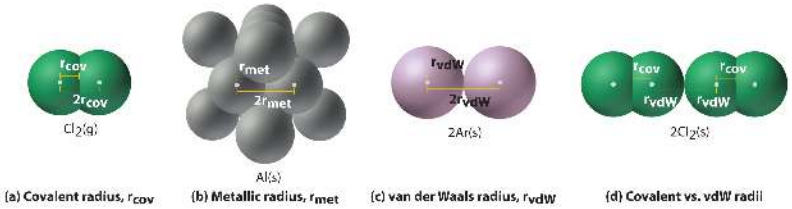


Figure 8.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent 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 8.3.2). 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 8.3.2). 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 8.3.2).

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. 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 8.3.3).

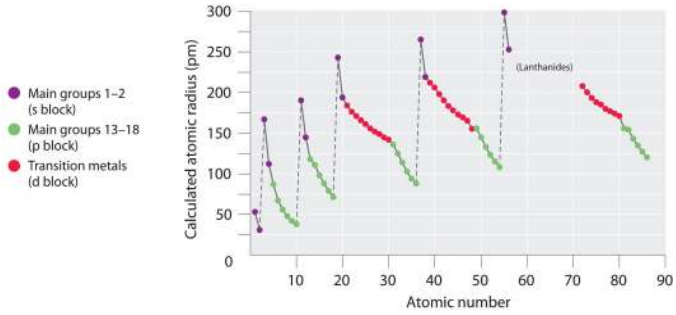


Figure 8.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

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 8.3.4).

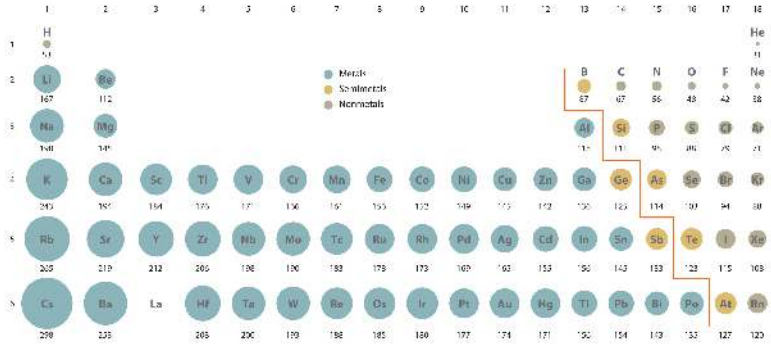


Figure 8.3.4 *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties.*

Note

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. 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.

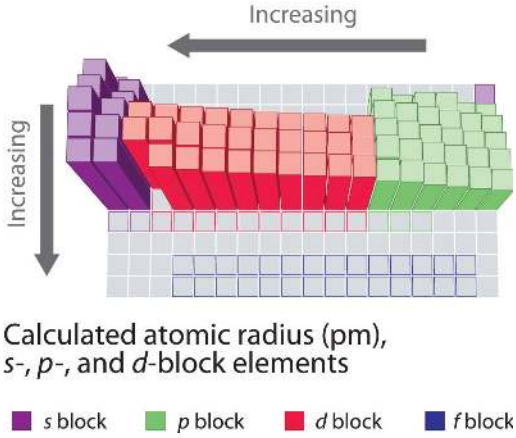


Figure 8.3.5: *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

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

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 8.3.1

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 8.3.1

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



Atomic Radius: https://youtu.be/ZYKB8SNrGVY

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 8.3.6, 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.

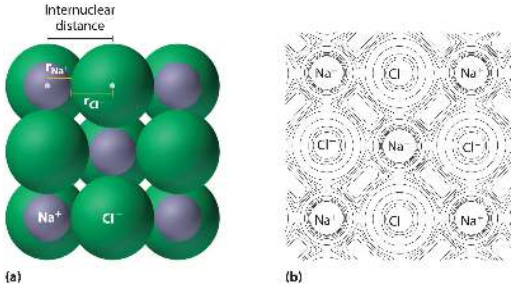


Figure 8.3.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for 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 8.3.7) *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).

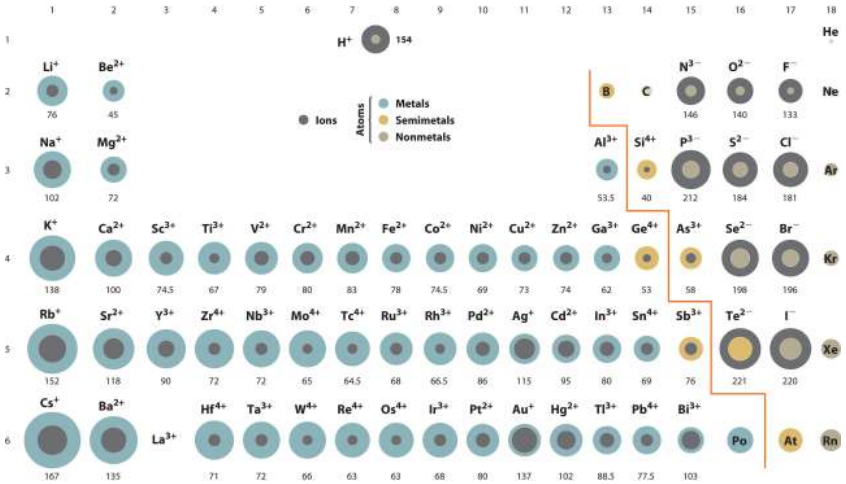


Figure 3.7. Source: Ionic radius data from R. D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note

Cations are **always** smaller than the neutral atom, and anions are **always** larger.

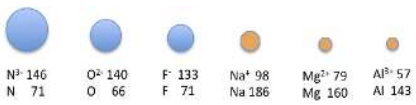
Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 8.3.1. 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 8.3.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^22s^22p^6$	$1s^22s^22p^63s^1$	$1s^22s^22p^63s^2$
Radius (pm)	102	154*	202†
*The metallic radius measured for Na(s).			
†Source: M. J. Wagner and J. L. Dye, “Alkalides, Electrides, and Expanded Metals,” Annual Review of Materials Science 23 (1993): 225–253.			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of n lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an isoelectronic series. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^22s^22p^6$) is shown in Table 7.3



https://chem.libretexts.org/@go/page/37025

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. The neon atom in this isoelectronic series is not listed in Table 8.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 9.3.3 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.

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

Example 8.3.2

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 8.3.2

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

- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

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.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

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8.4: Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{8.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 9.4.1. Larger values of *I* mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{8.4.2}$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an *n*th ionization energy (I_n) according to the following reactions:

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_1 = \text{1st ionization energy} \tag{8.4.3}$$

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_2 = \text{2nd ionization energy} \tag{8.4.4}$$

$$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^- \qquad I_3 = \text{3rd ionization energy} \tag{8.4.5}$$

Values for the ionization energies of Li and Be listed in Table 8.4.1 show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Note

Successive ionization energies for an element **increase** steadily.

Table 8.4.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	I (8.4.6)	Reaction	Electronic Transition	I (8.4.7)
$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$Be_{(g)} \rightarrow Be^+_{(g)} + e^-$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$Be^+_{(g)} \rightarrow Be^{2+}_{(g)} + e^-$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$Be^{3+}_{(g)} \rightarrow Be^{4+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The most important consequence of the values listed in Table 8.4.1 is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{8.4.8}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{8.4.9}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Note

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 8.4.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 8.4.2. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 8.4.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	579.4.4	1816.7	2744.8	**11,579.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1909.4.4	2914.1	4963.6	6274.0	**21,269.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,109.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3

*Inner-shell electron

Example 8.4.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.
b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^- \tag{8.4.10}$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

? Exercise 8.4.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer: Sr

The first column of data in Table 8.4.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

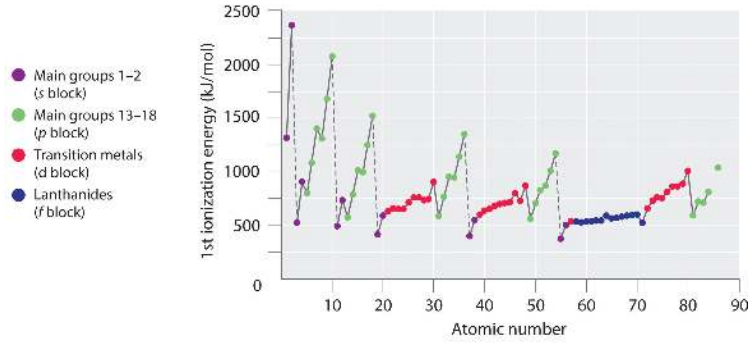


Figure 8.4.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

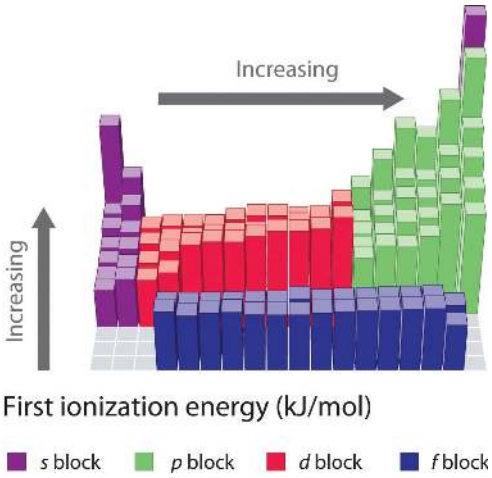


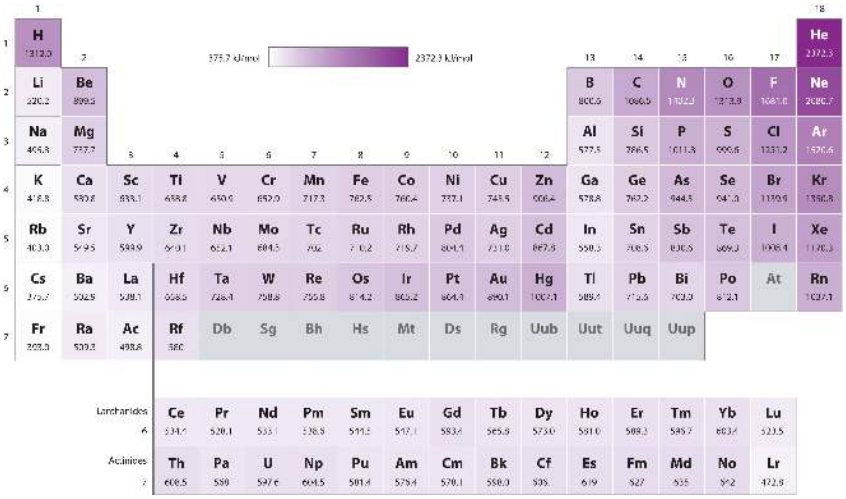
***Figure* 8.4.2:** *First Ionization Energies of the s-, p-, d-, and f-Block Elements*

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 8.4.1 and are presented numerically and graphically in Figure 8.4.2. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12) electron configurations.
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).

Note

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.



https://chem.libretexts.org/@go/page/37026

The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: [Ar]$4s^2 3d^{10} 4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the 4*p* subshell, screening the single 4*p* electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its [Ar]$3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as pseudo noble gas configurations. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the* $(n - 1)d^{10}$ *filled subshell*.

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the *ns* shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *ns*, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The [Ar]$3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

✔ Example 8.4.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

? Exercise 8.4.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer: As



Ionization Energy: https://youtu.be/k7j-u02ifzo

Summary

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

The tendency of an element to lose is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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8.5: Electron Affinity

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to adding an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA \tag{8.5.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad EA = -346\ kJ/mol \tag{8.5.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$Be_{(g)} + e^- \rightarrow Be^-_{(g)} \qquad EA \geq 0 \tag{8.5.3}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$N_{(g)} + e^- \rightarrow N^-_{(g)} \qquad EA \approx 0 \tag{8.5.4}$$

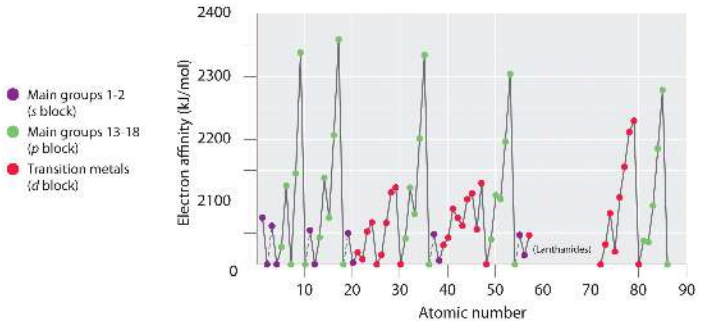


Figure 8.5.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table

Note

Generally, electron affinities become more negative across a row of the periodic table.

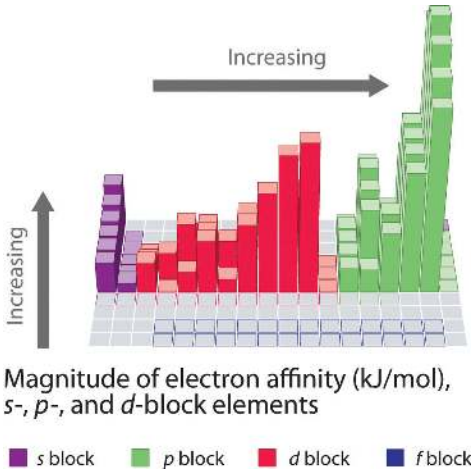
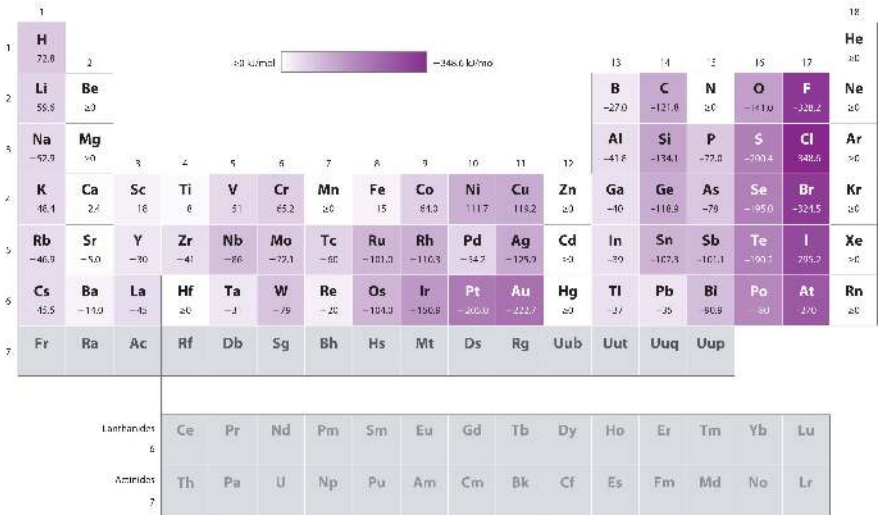


Figure 8.5.2 Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus. Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.



There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).

Note

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{8.5.5}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{8.5.6}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{8.5.7}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{8.5.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{8.5.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

Example 8.5.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 8.5.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer: Rb



Electron Affinity: https://youtu.be/M5MsRM2Xtds

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

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8.6: Magnetic Properties

Learning Objectives

- To predict the magnetic properties of atoms and molecules based on their electronic configurations.

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only paramagnetism, and diamagnetism are discussed here.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (that is best understood with molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



Video* 8.6.1*: *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video 8.6.1, since molecular oxygen (O_2 is paramagnetic, it is attracted to the magnet. In contrast, molecular nitrogen, N_2, has no unpaired electrons and it is diamagnetic (discussed below); it is therefore unaffected by the magnet.

Note

Paramagnetism is a form of magnetism whereby materials are **attracted** by an externally applied magnetic field.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net

magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 8.6.1.

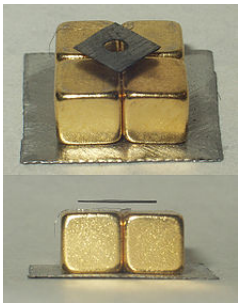


Figure 8.6.1: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

Note

Diamagnetic materials are **repelled** by the applied magnetic field.

Diamagnetism, to a greater or lesser degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show some other form of magnetism (such paramagntism), the diamagnetic contribution becomes negligible.

How to tell if a substance is paramagnetic or diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more electrons unpaired) or diamagnetic (all electrons paired)



Determining Magnetic Properties from Orbital Diagrams: https://youtu.be/lun_w5VKD8k

Example 8.6.1: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

Solution

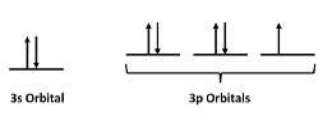
Follow the four steps outlines above.

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Since there is an unpaired electron, Cl atoms are paramagnetic (but weakly since only one electron is unpaired).

Exercise 8.6.1

Indicate whether boron atoms are paramagnetic or diamagnetic.

Answer:

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Example 8.6.2: Zinc Atoms

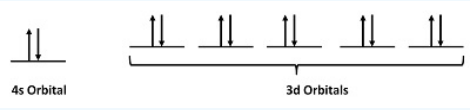
Are zinc atoms paramagnetic or diamagnetic?

Solution

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

Exercise 8.6.2

Indicate whether F^- ions are paramagnetic or diamagnetic.

Answer

The F^- ion has $2s^2 2p^6$ has the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Problems

1. How many unpaired electrons are found in oxygen atoms ?
2. How many unpaired electrons are found in bromine atoms?
3. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answers

1. The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.
2. The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.
3. The Fe^{2+} ion has $3d^6$ has the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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8.7: Periodic Properties of the Elements

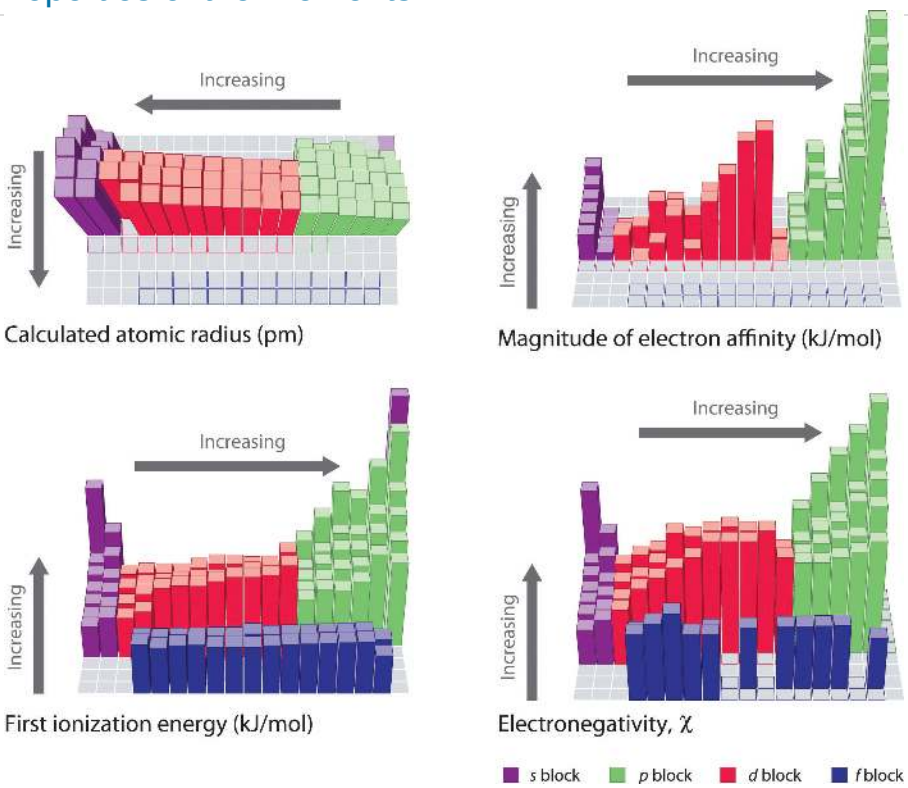


Figure 8.7.1 Summary of Major Periodic Trends. The general trends for the first ionization energy, electron affinity, and electronegativity are opposite to the general trend for covalent atomic radius.

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CHAPTER OVERVIEW

9: Chemical Bonding I: Basic Concepts

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We defined a chemical bond as the force that holds atoms together in a chemical compound. We also introduced two idealized types of bonding: **covalent bonding**, in which electrons are shared between atoms in a molecule or polyatomic ion, and **ionic bonding**, in which positively and negatively charged ions are held together by electrostatic forces. The concepts of covalent and ionic bonding were developed to explain the properties of different kinds of chemical substances.

Topic hierarchy

9.1: Lewis Theory: An Overview
9.2: Covalent Bonding: An Introduction
9.3: Polar Covalent Bonds and Electrostatic Maps
9.4: Writing Lewis Structures
9.5: Resonance
9.6: Exceptions to the Octet Rule
9.7: The Shapes of Molecules
9.8: Bond Order and Bond Lengths
9.9: Bond Energies

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9.1: Lewis Theory: An Overview

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

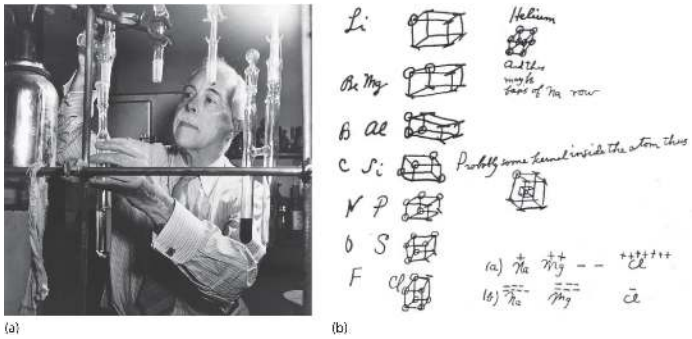


Figure 9.1.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

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 symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Note

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

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. For example, the electron configuration for atomic sulfur is $[Ne]3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

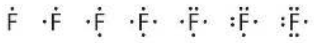


Figure 9.1.2.

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 9.1.2. 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.

Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li•
Be	[He]$2s^2$	•Be•
B	[He]$2s^2 2p^1$	•B•
C	[He]$2s^2 2p^2$	•C•
N	[He]$2s^2 2p^3$	•N:
O	[He]$2s^2 2p^4$	:O:
F	[He]$2s^2 2p^5$	:F:
Ne	[He]$2s^2 2p^6$	:Ne:

Figure 9.1.2: Lewis Dot Symbols for the Elements in Period 2

The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory.

The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

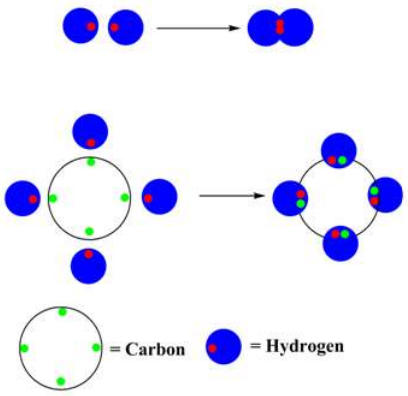


Figure 1: Bonding in H_2 and methane (CH_4)

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

Note

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 1: Salt

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

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 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.

Note

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.



Lewis Theory of Bonding: https://youtu.be/TZ6C5_k-SPs

Summary

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

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.

Contributors and Attributions

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9.2: Covalent Bonding: An Introduction

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. The general properties of Ionic substances are:

- usually brittle
- high melting point
- organized into an ordered lattice of atoms, which can be cleaved along a smooth line

However, the vast majority of chemical substances are ***not ionic*** in nature. G.N. Lewis reasoned that an atom might attain a noble gas electron configuration by ***sharing*** electrons

Note

A chemical bond formed by sharing a pair of electrons is called a covalent bond

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 9.2.1):

- 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 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.

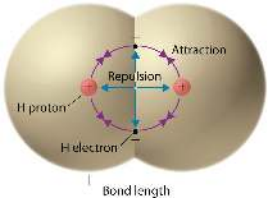


Figure 9.2.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 9.2.2) 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 9.2.2 and Figure 8.1, 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.

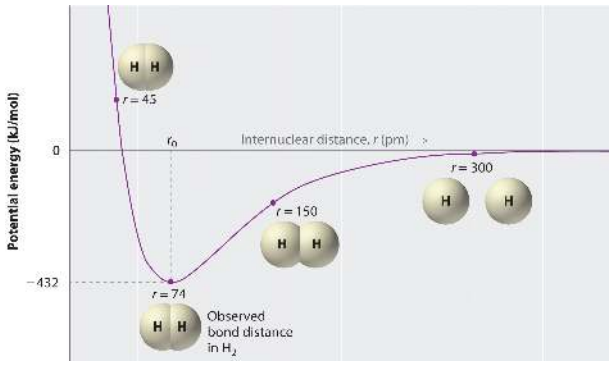


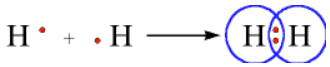
Figure 9.2.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

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.

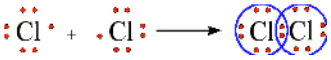
Lewis Structures

Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, Lewis dot formulas, Lewis dot structures, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:



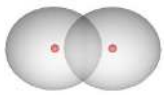
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1*s*) orbital. In a sense, each hydrogen atoms has the electron configuration of the noble gas helium (the octet rule). When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:



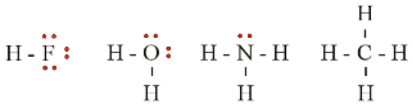
Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them. Examples of hydride compounds of the above elements (covalent bonds with hydrogen:



Multiple bonds

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***
- Three electron pairs shared a ***triple bond***



Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms and the N - N bond distance in N_2 is 1.10 Å (fairly short). From a study of various Nitrogen containing compounds bond distance as a function of bond type can be summarized as follows:

- N–N: 1.47Å
- N=N: 1.24Å
- N : =N :1.10Å

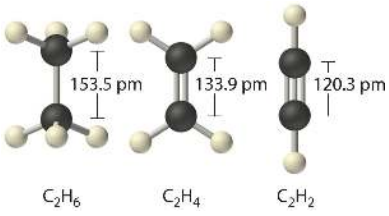
For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

Element	Group	Valence electrons	Bonds needed to form valence octet
F	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4



Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

Thus, the Lewis bonds successfully describe the covalent interactions between various nonmetal elements. 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. 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 9.2.1, 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 8.5, 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 9.2.1: 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.

Note

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases



Bond Lengths: https://youtu.be/9xn04FNkq9I

The Relationship between Bond Order & Bond Energy

As shown in Table 9.2.1, 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 9.2.2: 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).

Table 9.2.2 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

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 9.2.1).
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 9.2.1. 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\[\ce{Cl\bond{-}Cl > Br\bond{-}Br > F\bond{-}F > I–I}\] Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

Note

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.
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, e..g, for the SO_4^{2-} ion. 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.

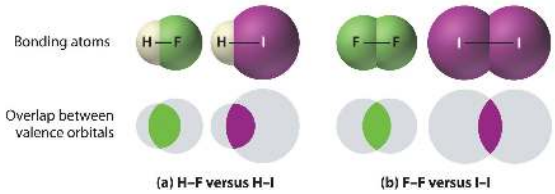


Figure 9.2.1 The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) 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.

Note

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 9.2.3); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 9.2.2 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 9.2.3: 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).

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{9.2.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_{3(l)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)} \tag{9.2.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

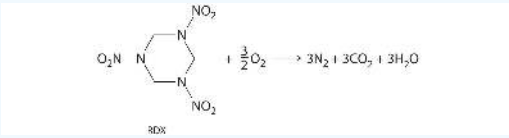
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

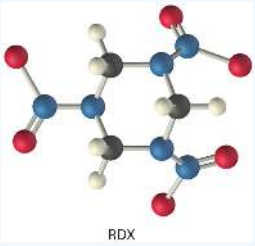
The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7 kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 9.2.1

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 9.2.2 to estimate the ΔH_{rxn} per mole of RDX.





Given: chemical reaction, structure of reactant, and Table 9.2.2.

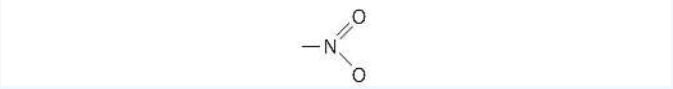
Asked for: ΔH_{rxn} per mole

Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
B. Use Equation 8.3.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group (–NO_2) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

B From Equation 8.3.1, we have

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{9.2.3}$$

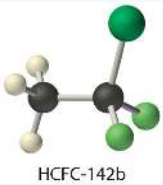
$$= 7962\ kJ/mol - 10,374\ kJ/mol \tag{9.2.4}$$

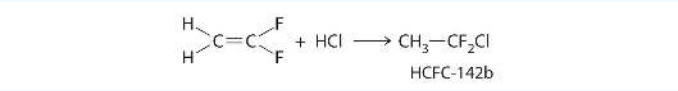
\[=−2412 \;kJ/mol]

Thus this reaction is also highly exothermic.

Exercise 9.2.1

The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:





Use tabulated bond energies to calculate ΔH_{rxn}.

Answer: −54 kJ/mol



Bond Energies: https://youtu.be/Prc6fbLXi5M

Summary

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

Formal charge on an atom:

$$\Delta H_{rxn} \approx \sum{\text{(bond energies of bonds broken)}}-\sum{\text{(bond energies of bonds formed)}} \label{8.3.1}$$

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.

Contributors and Attributions

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9.3: Polar Covalent Bonds and Electrostatic Maps

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the shared electron pairs is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. We demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure $9.3.2$ and Figure $9.3.2$). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Note

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **greater** the value, the **greater** the attractiveness for electrons.

Electronegativity is a function of: (1) the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and (2) the atom's ***electron affinity*** (how strongly the atom attracts other electrons). Both of these are properties of the *isolated* atom. An element that is will be *highly electronegative* has:

- a large (negative) electron affinity
- a high ionization energy (always endothermic, or positive for neutral atoms)

and will

- attract electrons from other atoms
- resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

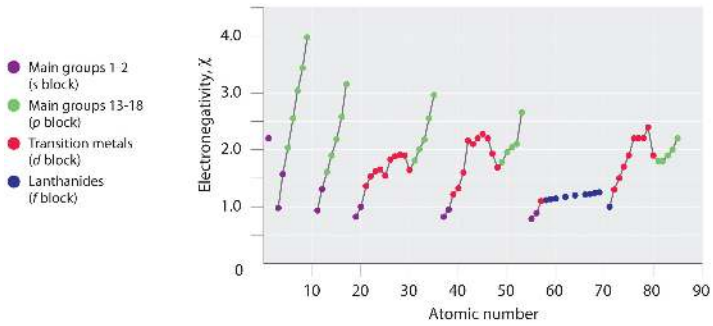


Figure 9.3.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Periodic variations in Pauling's electronegativity values are illustrated in Figure 9.3.1 and Figure 9.3.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

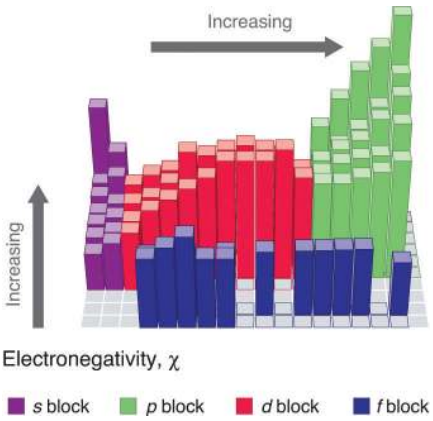
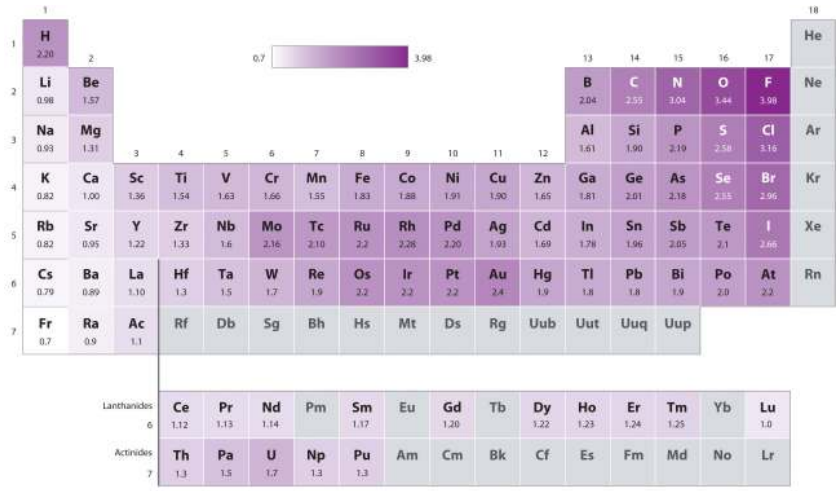


***Figure* 9.3.2:** *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem (e.g., the Mulliken electronegativity scale).

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **semimetals** (or metalloids), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 9.3.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

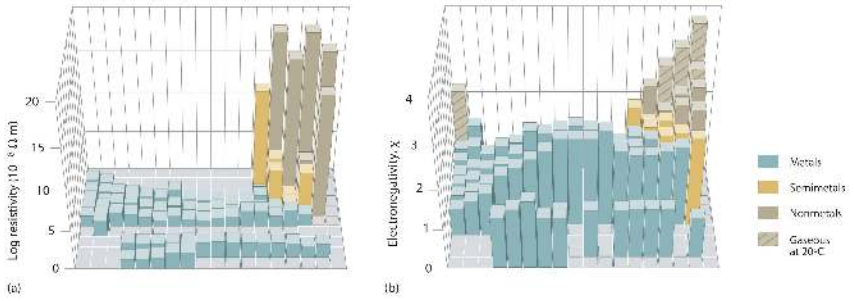


Figure 9.3.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Note

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

Example 9.3.1

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

<p">**Strategy:**

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 9.3.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

Exercise 9.3.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Answer: Rb < Zr < Ge < N < O; metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)



Electronegativity: https://youtu.be/3Pe0iShCdhM

Percent Ionic Character of a Covalent polar bond

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, which means that electrons are shared unequally between the bonded atoms. Figure 9.3.4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded

atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

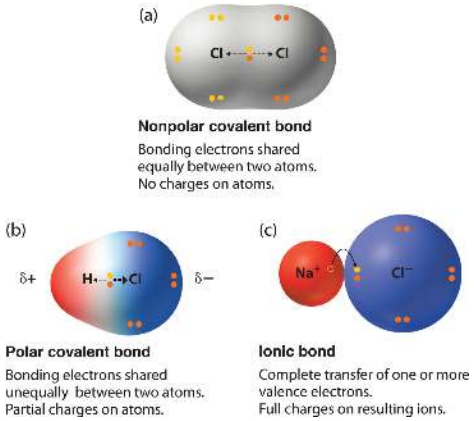


Figure 9.3.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely 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. Electronegativity (χ) 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 (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\text{less electronegative}}{A} - \underset{\text{more electronegative}}{B}$$
$$\delta^+ \qquad\qquad \delta^-$$

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 9.3.2). 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

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

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

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 as a Measure of Bond Polarity

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:

$$\mu = Qr \tag{9.3.1}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot \cdot m \tag{9.3.2}$$

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 9.3.2).

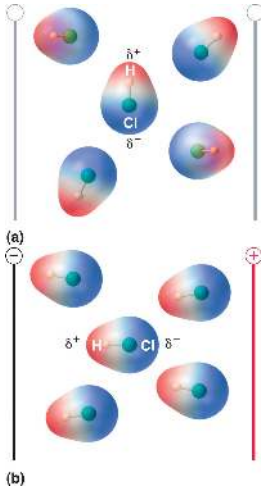


Figure 9.3.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end 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 10.3.2 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

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C \tag{9.3.3}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-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.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{9.3.4}$$

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

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} - \overset{0.18\delta^-}{Cl}$$

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 9.3.6 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 9.3.6 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 11.

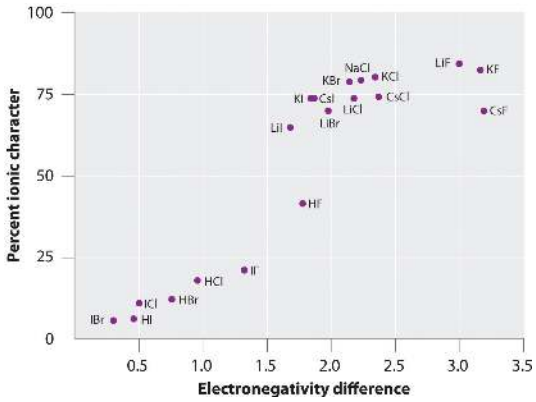


Figure 9.3.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 9.3.2

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 and Equation 10.3.2.

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

$$Q = \frac{\mu}{r} = 9.001 \ \cancel{D}\left(\frac{3.3356 \times 10^{-30} \ C \cdot \cancel{m}}{1 \ \cancel{D}}\right)\left(\frac{1}{236.1 \ \cancel{pm}}\right)\left(\frac{1 \ \cancel{pm}}{10^{-12} \ \cancel{m}}\right) = 1.272 \times 10^{-19} \ C \quad (9.3.5)$$

Thus NaCl behaves as if it had charges of 1.272×10^{-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):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{9.3.6}$$

? Exercise 9.3.2

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?

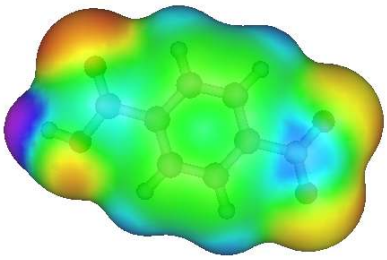
Answer: 55.5%



Dipole Intermolecular Force: https://youtu.be/ACq_95SIBck

Electrostatic Potential Maps

Electrostatic potential maps convey information about the charge distribution of a molecule because of the properties of the nucleus and nature of electrostatic potential energy. A region of higher than average electrostatic potential energy indicates the presence of a stronger positive charge or a weaker negative charger. Given the positive charge of the nuclei, the higher potential energy value indicates the absence of negative charges (less screening of the nuclei), which would mean that there are fewer electrons in this region. The converse is also true with a low electrostatic potential indicateing an abundance of electrons. This property of electrostatic potentials can be extrapolated to molecules as well.



Note: Constructing a Electrostatic Potential Map

The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons, at a particular position. To accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic

potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.

The most important thing to consider when analyzing an electrostatic potential map is the charge distribution. The relative distributions of electrons will allow you to deduce everything you need to know from these maps. Recall the relationship between electrostatic potential and charge distribution. Areas of low potential, red, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Oxygen has a higher electronegativity value than sulfur (Table A2), hence. oxygen atoms would have a higher electron density around them than sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. Now note that there are two oxygen atoms in sulfur dioxide (Figure 9.3.7). There are two sphere shaped objects that have red regions. These areas correspond to the location of the oxygen atoms. The blue tainted sphere at the top corresponds to the location of the sulfur atom.

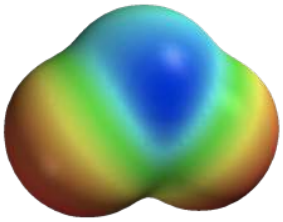


Figure 9.3.7. The electrostatic diagram of Sulfur Dioxide (SO_2). Which parts of this diagram correlate to the respective atomic components? Red indicates the lowest electrostatic potential energy, and blue indicates the highest electrostatic potential energy. Intermediary colors represent intermediary electrostatic potentials.

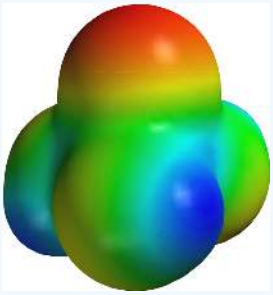
Note

A high electrostatic potential indicates the relative **absence** of electrons and a low electrostatic potential indicates an **abundance** of electrons

Electrostatic potential maps can also be used to determine the nature of the molecules chemical bond. Consider SO_2 in Figure 9.3.7, there is a great deal of intermediary potential energy, the non red or blue regions, in this diagram. This indicates that the electronegativity difference is not very great. In a molecule with a great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity difference. Note that the electronegativity difference is a key determinant in the nature of a chemical bond.

Example 9.3.3

The following electrostatic potential map of phosphoric acid $\backslash H_3PO_4$. What regions correspond to atoms of oxygen, hydrogen, and phosphorous respectively?



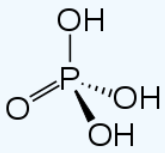
Solution

You do not need to know the molecular structure to answer this question. You do need to know the relative electronegative values of these atoms (Table A4).

- Oxygen has the greatest electronegative value,
- Phosphorous the second most, and
- Hydrogen has the smallest electronegative value.

Simply by knowing this, you can deduce that oxygen would be affiliated with the red region or redish regions of the diagram, and hydrogen would be affiliated with the blue region. Phosphorous would fall in between these two extremes, in the green region.

Here is the molecular diagram of phosphoric acid:



Summary

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

Dipole moment

$$\mu = Qr \label{10.3.2}$$

The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

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.

9.3: Polar Covalent Bonds and Electrostatic Maps is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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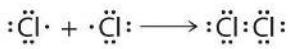
9.4: Writing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

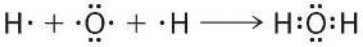
Using Lewis Dot Symbols to Describe Covalent Bonding

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; the other three pairs of electrons on each chlorine atom are called lone pairs. 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 bond. Examples of this type of bonding are presented in Section 8.6 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.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall 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 will explain later 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.

Note

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

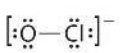
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each 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.

The OCl^- Ion

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.

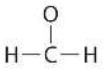
The CH_2O Molecule

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:



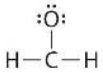
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

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.

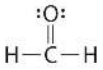
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



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 9.4.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

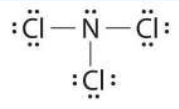
Asked for: Lewis electron structures

Strategy:

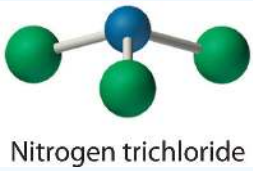
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

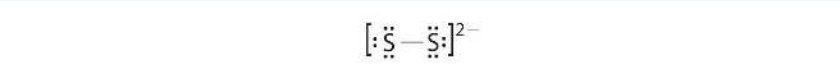
1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl 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:



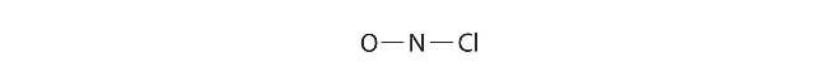
Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



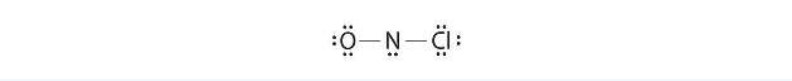
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons 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:

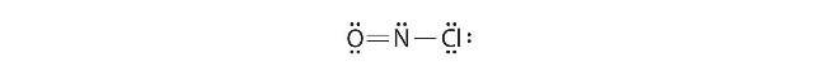


Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:

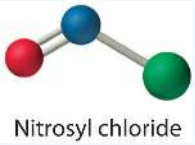


Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in

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:



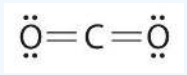
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



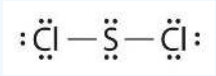
Exercise 9.4.1

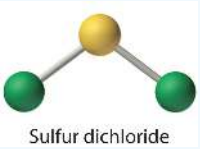
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer

1. 



2. 



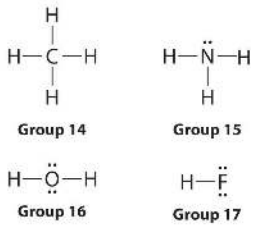


Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

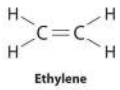
Using Lewis Electron Structures to Explain Stoichiometry

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 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



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.



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.

Note

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

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 9.4.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

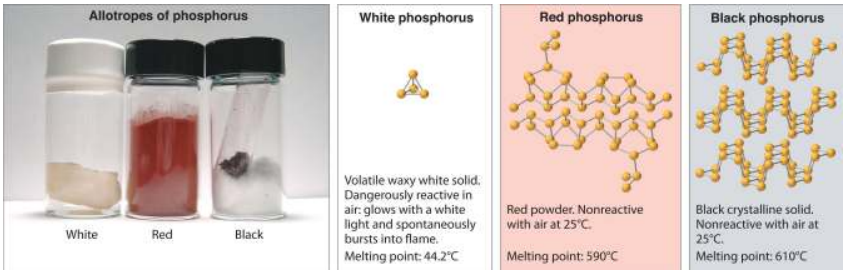


***Figure* 9.4.3**: *The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black 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 charge 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.

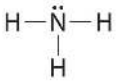
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- 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:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)} \quad \text{(atom in Lewis structure)}$$

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 8.5.2, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \qquad (9.4.1)$$

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 8.5.2 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \qquad (9.4.2)$$

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.

Note

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

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.



Lewis Structure of Charged Molecules: https://youtu.be/pTkziPtvMYU

Example 9.4.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

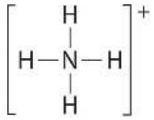
Asked for: formal charges

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 8.5.2 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



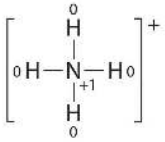
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 8.5.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0 \tag{9.4.3}$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0 \tag{9.4.4}$$

The formal charges on the atoms in the NH_4^+ ion are thus

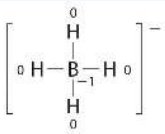


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 9.4.2

Write the formal charges on all atoms in BH_4^-.

Answer



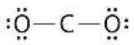
If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable 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.

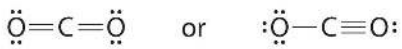
CO_2

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:

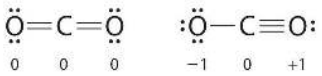


This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

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 Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 9.4.3: The Thiocyanate Ion

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

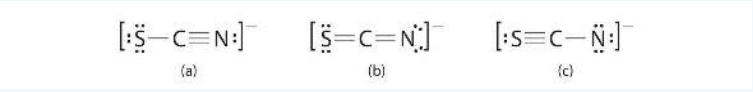
Asked for: Lewis electron structures, formal charges, and preferred arrangement

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 8.5.1.
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:



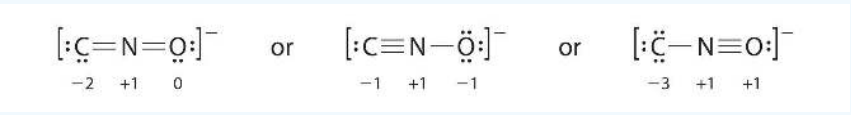
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, 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 9.4.3: The Fulminate Ion

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.

Summary

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

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.

Contributors and Attributions

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9.5: Resonance

Learning Objectives

- To understand the concept of resonance.

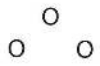
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds.

When one Lewis Structure is not enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). 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°.

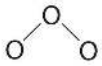
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



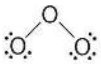
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



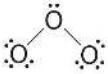
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

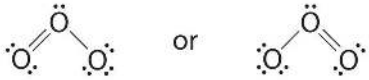


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



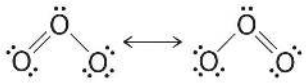
6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



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, 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. 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:



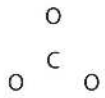
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> **Note**
>
> When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the *average* of the resonance structures.

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:

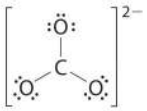


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

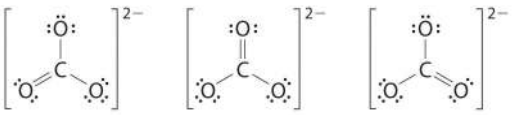


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

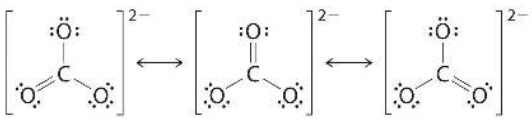


5. No electrons are left for the central atom.

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:

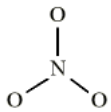


The actual structure is an average of these three resonance structures.

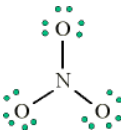
The Nitrate (NO_3^-) ion

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

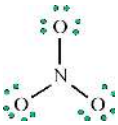
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

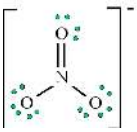


4. Place any leftover electrons (24-24 = **0**) on the center atom:



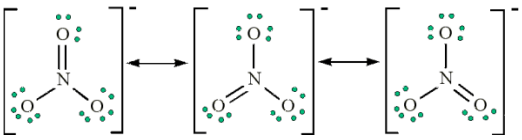
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond

Example 9.5.1: Benzene

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

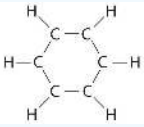
Asked for: resonance structures

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.

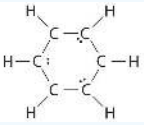
Solution:

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:



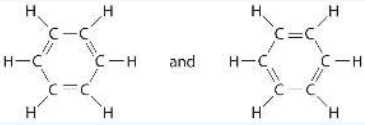
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

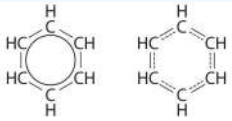


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



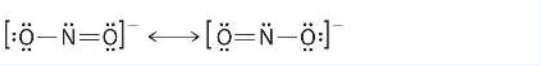
Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in 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

? Exercise 9.5.1: Nitrate Ion

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.



Resonance Structures: https://youtu.be/aSP0D72MKe4

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. 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. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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9.6: Exceptions to the Octet Rule

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide (NO ,refer to figure one). Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in.*

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitrogen monoxide. Nitrogen monoxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitrogen monoxide had ten valence electrons we would come up with the Lewis Structure (Figure 9.6.1):

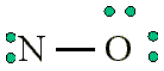


Figure 9.6.1: This is if Nitrogen monoxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure 9.6.2 based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure 9.6.1, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure 9.6.1, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitrogen monoxide (Figure 9.6.2):

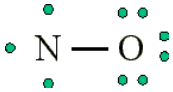


Figure 9.6.2: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, odd Number of Valence Electrons will result in the molecule being paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one was to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure 9.6.3):

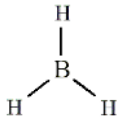


Figure 9.6.3

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure 9.6.4).

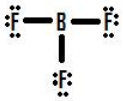


Figure 9.6.4

If you look Figure 9.6.4, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure 9.6.5):

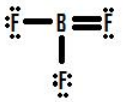


Figure 9.6.5

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure 9.6.5, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure 9.6.6:

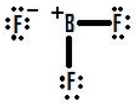


Figure 9.6.6

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure 9.6.4), the one with the double bond (Figure 9.6.5), and the one with the ionic bond (Figure 9.6.6). The most contributing structure is probably the incomplete octet structure (due to Figure 9.6.5 being basically impossible and Figure 9.6.6 not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

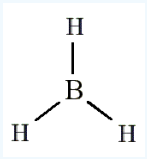
Example 9.6.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

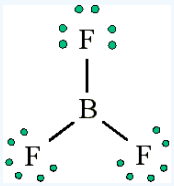
Solution

1. Add electrons (3*7) + 3 = **24**

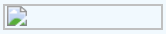
2. Draw connectivities:



3. Add octets to outer atoms:

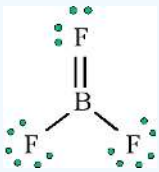


4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

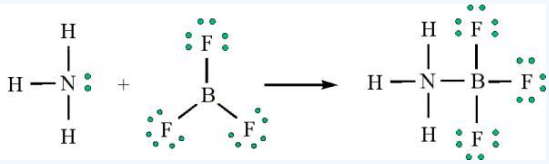


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

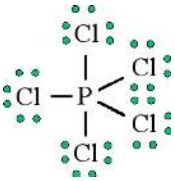
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



Exception 3: Expanded Valence Shells

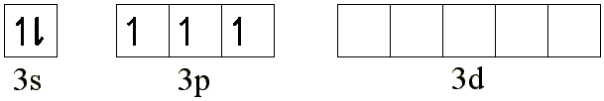
More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



Note

Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.

Example 9.6.2: The SO_4^{-2} ion

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

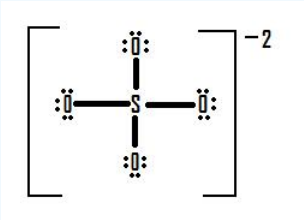


Figure 9.6.12

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

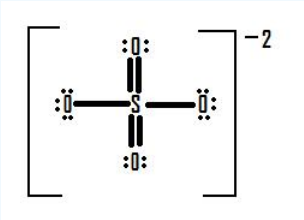


Figure 9.6.13

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure 9.6.12, as opposed to +2 and -1 (difference of 3) in Figure 9.6.12) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

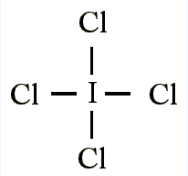
Example 9.6.3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

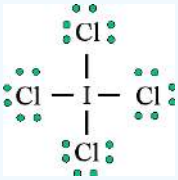
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

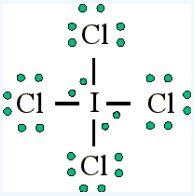
2. Draw the connectivities:



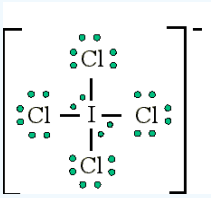
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.



Expanded Valence Shell Bonding: https://youtu.be/Y4fBdOJBSHI

Outside links

- http://www.saskschools.ca/curr_content/chem20/covmolec/exceptns.html
- student.ccbcmd.edu/~cyau1/121...ctetSp2006.pdf
- http://www.youtube.com/watch?v=KEQw9uQ8fUU
- www.rice.edu/~jenky/sports/antiox.html

References

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

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9.7: The Shapes of Molecules

The Learning Objectives of this Module:

1. To use the VSEPR model to predict molecular geometries.
2. To predict whether a molecule has a dipole moment.

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. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced "vesper"), which can be used 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.

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.

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 9.1 and Figure 9.2.

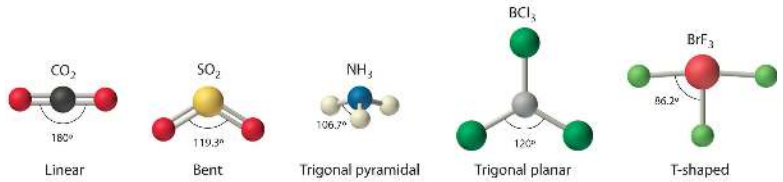


Figure 9.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms

The VSEPR model explains these differences in molecular geometry.

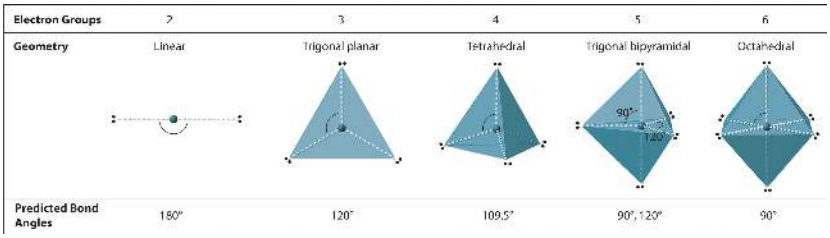


Figure 9.2 *Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.*

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. Using this information, we can describe the molecular geometry, 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 9.2 and Figure 9.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

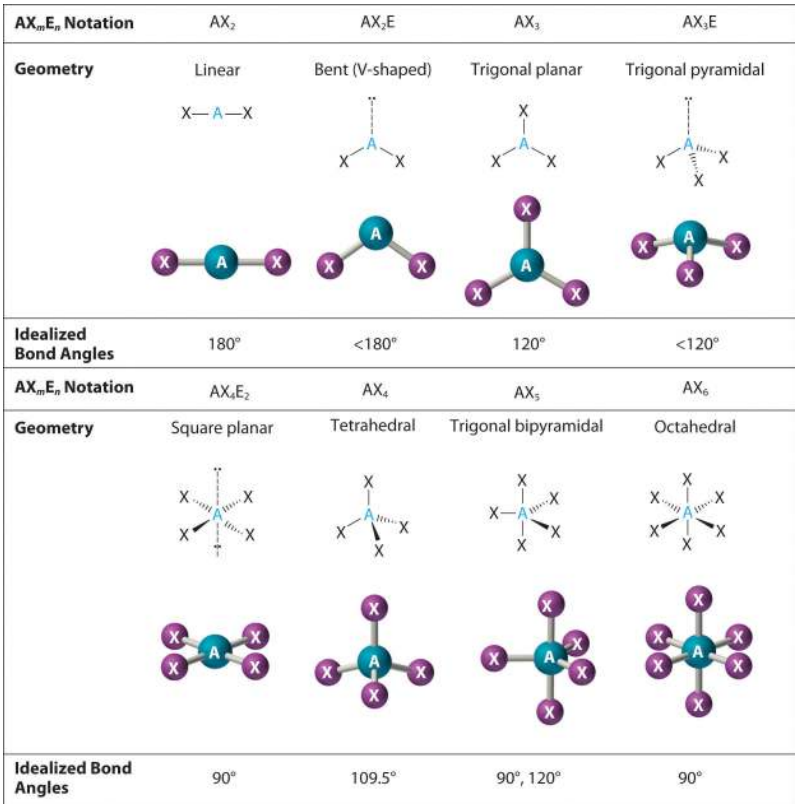


Figure 9.3 Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.

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

H:Be:H or H—Be—H

Lewis structure

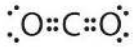
2. There are two electron groups around the central atom. We see from Figure 9.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 9.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

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.

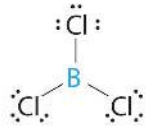
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

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 9.3). The structure of CO_2 is shown in Figure 9.1.

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

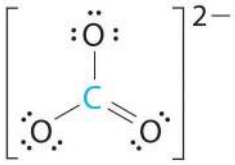
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 9.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 9.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 9.1.

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 previously, the Lewis electron structure of one of three resonance forms is represented as

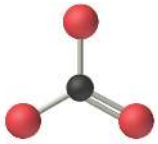


Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $1\frac{1}{3}$. We minimize repulsions by placing the three groups 120° apart (Figure 9.2).

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 9.3 that the molecular geometry of CO_3^{2-} is trigonal planar.

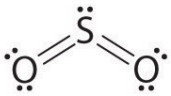


Molecular geometry
(trigonal planar)

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 9.2).

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 9.4). 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 9.1 and Figure 9.3).

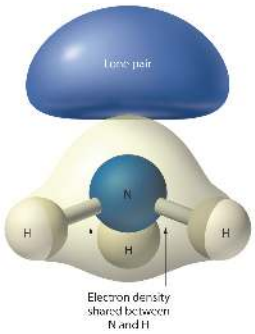
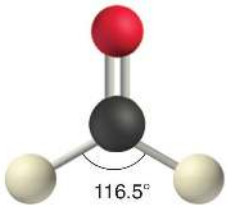


Figure 9.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

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

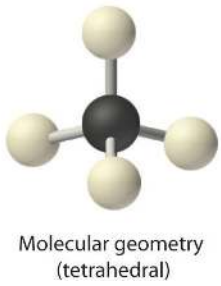


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 9.2, 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.

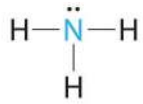
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 9.3).



Molecular geometry
(tetrahedral)

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

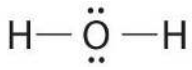
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

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 9.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 9.3 and Figure 9.4).

AX_2E_2: H_2O

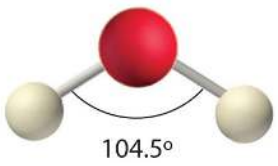
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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 9.2.

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.

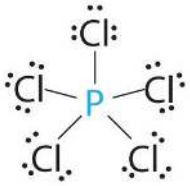


Five Electron Groups

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

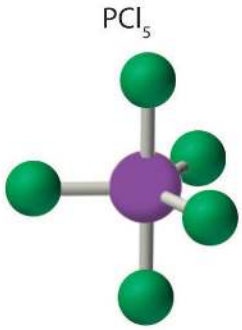
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



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 9.2):

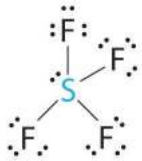
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 9.3. 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



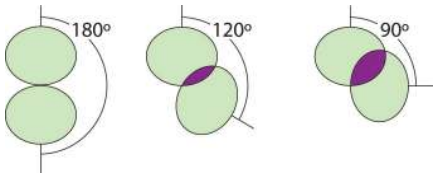
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

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 9.2.

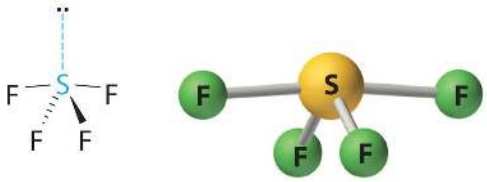
3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the 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 9.5 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.

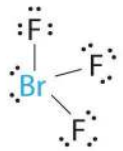
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



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

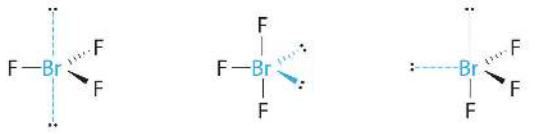


Lewis structure

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. 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 9.1).

Note
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.

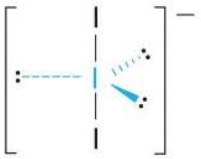
AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



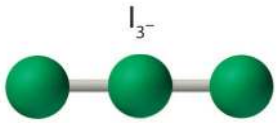
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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.

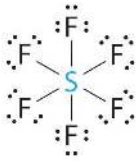


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 9.2.)

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



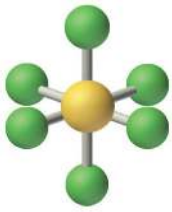
Lewis structure

With an expanded valence, that this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 9.2 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.

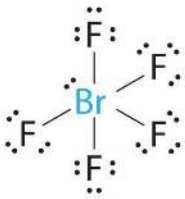
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E: BrF_5

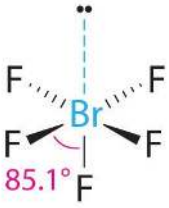
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

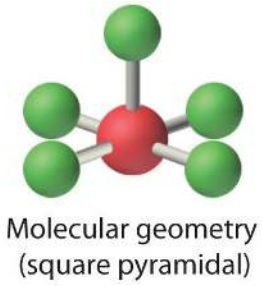
With its expanded valence, this species is an exception to the octet rule.

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:



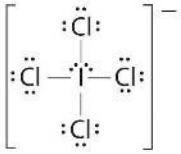
3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ 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.

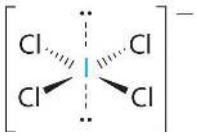


AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

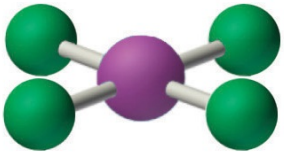


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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 ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



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 9.6.

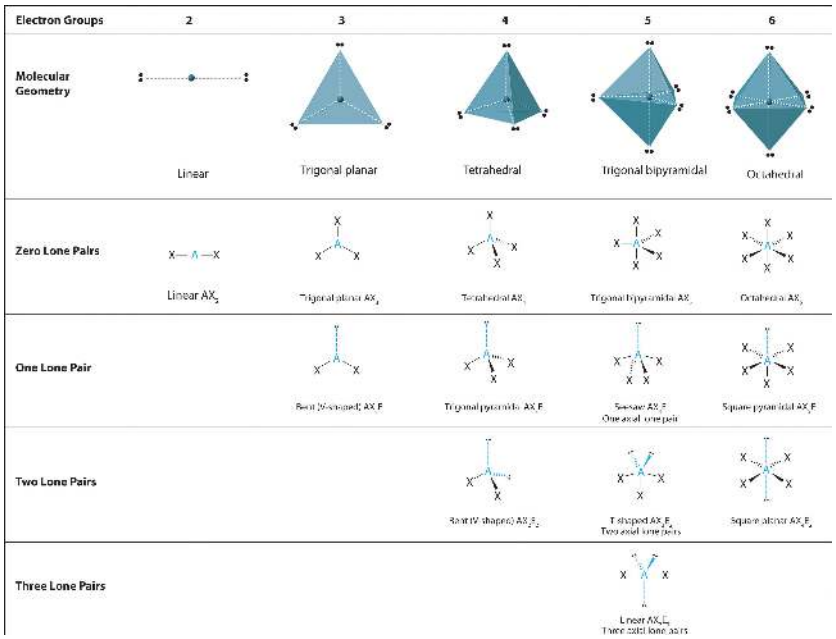


Figure 9.6 Overview of Molecular Geometries

Example 1

https://chem.libretexts.org/@go/page/37038

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.

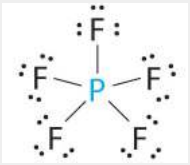
B. Determine the electron group arrangement around the central atom that minimizes repulsions.

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:

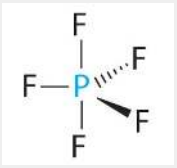
1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



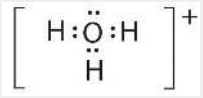
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 9.6).

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this 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.



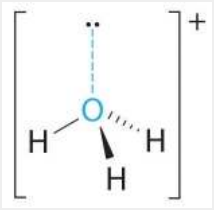
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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.

a. XeO_3

b. PF_6^-

c. NO_2^+

Answer

a. trigonal pyramidal

b. octahedral

c. linear

Example 2

https://chem.libretexts.org/@go/page/37038

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.

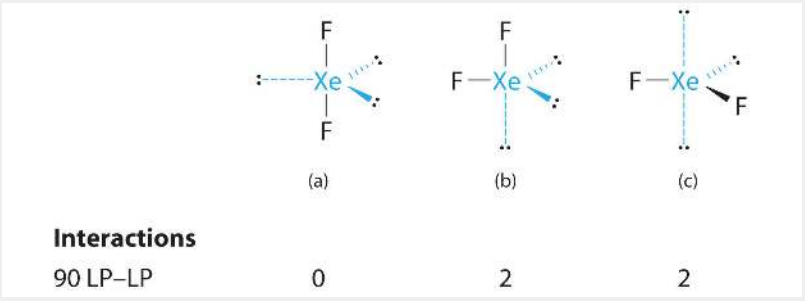
Solution:

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.

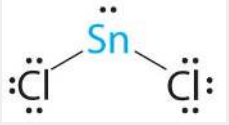
C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



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 2

Predict the molecular geometry of each molecule.

a. SO_3

b. XeF_4

Answers:

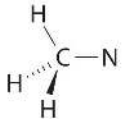
a. trigonal planar

b. square planar

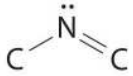
Molecules with No Single Central Atom

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:

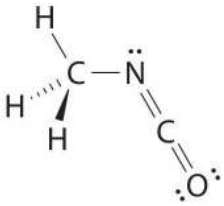


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



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 9.7).

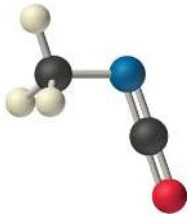


Figure 9.7: *The Experimentally Determined Structure of Methyl Isocyanate*

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 3

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 9.3 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 Dipole Moments

You previously 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 9.8). 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 9.8); 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.

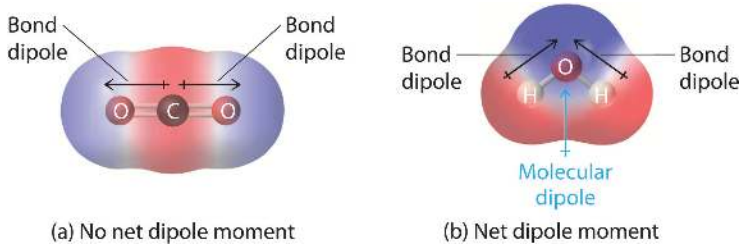


Figure 9.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 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 9.9. 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.

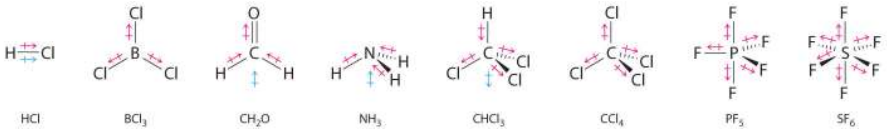


Figure 9.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

Note

Molecules with asymmetrical charge distributions have a net dipole moment.

Example 4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

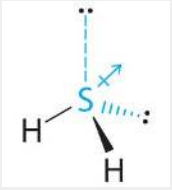
Asked for: net dipole moment

Strategy:

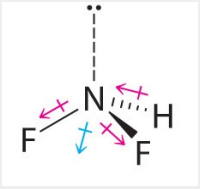
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

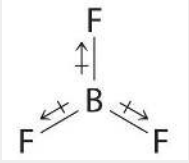
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 9.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole 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?

- 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.
- 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?
- 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.
- How is molecular geometry related to the presence or absence of a molecular dipole moment?
- How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?

- 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.
- When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
- 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
- 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?
- Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.
- 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

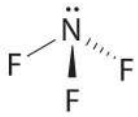
4. TeF_4
5. CH_3OH
6. XeO_4

9. Of the molecules $Cl_2C{=}Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.

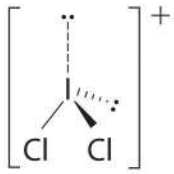
10. Of the molecules SO_3, XeF_4, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

Answers

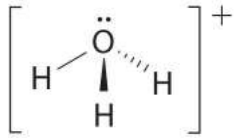
1. 1. trigonal planar (all electron groups are bonding pairs)
   2. tetrahedral (one lone pair on P)
   3. trigonal bipyramidal (three lone pairs on Xe)
   4. tetrahedral (all electron groups on Al are bonding pairs)
   5. tetrahedral (all electron groups on C are bonding pairs)
2.
3. 1. four electron groups, linear molecular geometry
   2. four electron groups, pyramidal molecular geometry

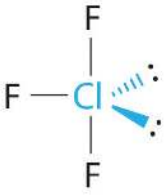


   3. four electron groups, bent molecular geometry



   4. two electron groups, linear molecular geometry
   5. four electron groups, pyramidal molecular geometry

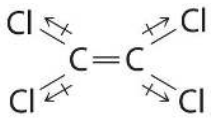


4.
5. 

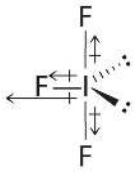
   The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

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.



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9.8: Bond Order and Bond Lengths

Bond order is the number of chemical bonds between a pair of atoms and indicates the stability of a bond. For example, in diatomic nitrogen, N≡N, the bond order is 3; in acetylene, H−C≡C−H, the carbon-carbon bond order is also 3, and the C−H bond order is 1. Bond order and bond length indicate the type and strength of covalent bonds between atoms. Bond order and length are inversely proportional to each other: when bond order is increased, bond length is decreased.

Introduction

Chemistry deals with the way in which subatomic particles bond together to form atoms. Chemistry also focuses on the way in which atoms bond together to form molecules. In the atomic structure, electrons surround the atomic nucleus in regions called orbitals. Each orbital shell can hold a certain number of electrons. When the nearest orbital shell is full, new electrons start to gather in the next orbital shell out from the nucleus, and continue until that shell is also full. The collection of electrons continues in ever widening orbital shells as larger atoms have more electrons than smaller atoms. When two atoms bond to form a molecule, their electrons bond them together by mixing into openings in each others' orbital shells. As with the collection of electrons by the atom, the formation of bonds by the molecule starts at the nearest available orbital shell opening and expand outward.

Bond Order

Bond order is the number of bonding pairs of electrons between two atoms. In a covalent bond between two atoms, a single bond has a bond order of one, a double bond has a bond order of two, a triple bond has a bond order of three, and so on. To determine the bond order between two covalently bonded atoms, follow these steps:

1. Draw the Lewis structure.
2. Determine the type of bonds between the two atoms.
   - 0: No bond
   - 1: Single bond
   - 2: double bond
   - 3: triple bond

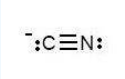
If the bond order is zero, the molecule cannot form. The higher bond orders indicate greater stability for the new molecule. In molecules that have resonance bonding, the bond order does not need to be an integer.

Example 9.8.1: CN^-

Determine the bond order for cyanide, CN^-.

Solution

1) Draw the Lewis structure.



2) Determine the type of bond between the two atoms.

Because there are 3 dashes, the bond is a triple bond. A triple bond corresponds to a bond order of 3.

Example 9.8.2: H_2

Determine the bond order for hydrogen gas, H_2.

Solution

1) Draw the Lewis structure.



2) Determine the type of bond between the two atoms.

There is only one pair of shared electrons (or dash), indicating is a single bond, with a bond order of 1.

Polyatomic molecules

If there are more than two atoms in the molecule, follow these steps to determine the bond order:

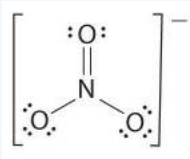
1. Draw the Lewis structure.
2. Count the total number of bonds.
3. Count the number of bond groups between individual atoms.
4. Divide the number of bonds between atoms by the total number of bond groups in the molecule.

Example 9.8.3: NO_3^-

Determine the bond order for nitrate, NO_3^-.

Solution

1) Draw the Lewis structure.



2) Count the total number of bonds.

4

The total number of bonds is 4.

3) Count the number of bond groups between individual atoms.

3

The number of bond groups between individual atoms is 3.

4) Divide the number of bonds between individual atoms by the total number of bonds.

$$\frac{4}{3} = 1.33 \tag{9.8.1}$$

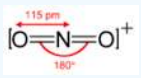
The bond order is 1.33

Example 9.8.4: NO_2^+

Determine the bond order for nitronium ion: NO_2^+.

Solution

1) Draw the Lewis Structure.



2) Count the total number of bonds.

4

The total number of bonds is 4.

3) Count the number of bond groups between individual atoms.

2

The number of bond groups between atoms is 2.

4) Divide the bond groups between individual atoms by the total number of bonds.

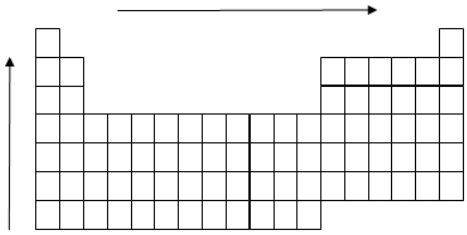
$$\frac{4}{2} = 2 \tag{9.8.2}$$

The bond order is 2.

A high bond order indicates more attraction between electrons. A higher bond order also means that the atoms are held together more tightly. With a lower bond order, there is less attraction between electrons and this causes the atoms to be held together more loosely. Bond order also indicates the stability of the bond. The higher the bond order, the more electrons holding the atoms together, and therefore the greater the stability.

Trends in the Periodic Table

Bond order increases across a period and decreases down a group.



Bond Length

Bond length is defined as the distance between the centers of two covalently bonded atoms. The length of the bond is determined by the number of bonded electrons (the bond order). The higher the bond order, the stronger the pull between the two atoms and the shorter the bond length. Generally, the length of the bond between two atoms is approximately the sum of the covalent radii of the two atoms. Bond length is reported in picometers. Therefore, bond length increases in the following order: triple bond < double bond < single bond.

To find the bond length, follow these steps:

1. Draw the Lewis structure.
2. Look up the chart below for the radii for the corresponding bond.
3. Find the sum of the two radii.

✔ 4

Determine the carbon-to-chlorine bond length in CCl_4.

Solution

Using Table A3, a C single bond has a length of 75 picometers and that a Cl single bond has a length of 99 picometers. When added together, the bond length of a C-Cl bond is approximately 174 picometers.

✔ 2

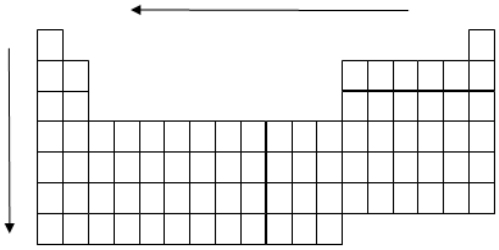
Determine the carbon-oxygen bond length in CO_2.

Solution

Using Table A3, we see that a C double bond has a length of 67 picometers and that an O double bond has a length of 57 picometers. When added together, the bond length of a C=O bond is approximately 124 picometers.

Trends in the Periodic Table

Because the bond length is proportional to the atomic radius, the bond length trends in the periodic table follow the same trends as atomic radii: bond length decreases across a period and increases down a group.



Problems

1. What is the bond order of O_2?
2. What is the bond order of NO_3^-?
3. What is the carbon-nitrogen bond length in HCN?
4. Is the carbon-to-oxygen bond length greater in CO_2 or CO?
5. What is the nitrogen-fluoride bond length in NF_3?

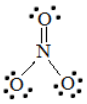
Solutions

1. First, write the Lewis structure for O_2.



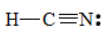
There is a double bond between the two oxygen atoms; therefore, the bond order of the molecule is 2.

2. The Lewis structure for NO_3^- is given below:



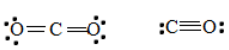
To find the bond order of this molecule, take the average of the bond orders. N=O has a bond order of two, and both N-O bonds have a bond order of one. Adding these together and dividing by the number of bonds (3) reveals that the bond order of nitrate is 1.33.

3. To find the carbon-nitrogen bond length in HCN, draw the Lewis structure of HCN.



The bond between carbon and nitrogen is a triple bond, and a triple bond between carbon and nitrogen has a bond length of approximately 60 + 54 =114 pm.

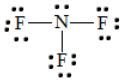
4. From the Lewis structures for CO_2 and CO, there is a double bond between the carbon and oxygen in CO_2 and a triple bond between the carbon and oxygen in CO.



Referring to the table above, a double bond between carbon and oxygen has a bond length of approximately 67 + 57 = 124 pm and a triple bond between carbon and oxygen has a bond length of approximately 60 + 53 =113 pm. Therefore, the bond length is greater in CO_2.

Another method makes use of the fact that the more electron bonds between the atoms, the tighter the electrons are pulling the atoms together. Therefore, the bond length is greater in CO_2.

5. To find the nitrogen-to-fluorine bond length in NF_3, draw the Lewis structure.



The bond between fluorine and nitrogen is a single bond. From the table above, a single bond between fluorine and nitrogen has a bond length of approximately 64 + 71 =135 pm.

References

1. Campbell, Neil A., Brad Williamson, and Robin J. Heyden. Biology: Exploring Life. Boston, Massachusetts: Pearson Prentice Hall, 2006.
2. Petrucci, Ralph H., Harwood, William S., Herring, F. G., and Madura Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey: Pearson Education, Inc., 2007. Print.
3. Cordero, Beatriz, Verónica Gómez, Ana E. Platero-Prats, Marc Revés, Jorge Echeverría, Eduard Cremades, Flavia Barragán and Santiago Alvarez. Dalton's Transactions." Covalent radii revisited 2008:
4. Pekka Pyykkö and Michiko Atsumi, Chem. Eur. J. Molecular Double-Bond Covalent Radii for Elements Li–E112 2009

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9.9: Bond Energies

Learning Objectives

- The define Bond-dissociation energy (bond energy)
- To correlate bond strength with bond length
- To define and used *average bond energies*

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. The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together.

The Relationship between Bond Order and Bond Energy

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 9.9.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 9.9.1: 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 8.11).
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 8.11. 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

$$\mathrm{Cl–Cl} > \mathrm{Br–Br} > \mathrm{F–F} > \mathrm{I–I}$$

Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> 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.

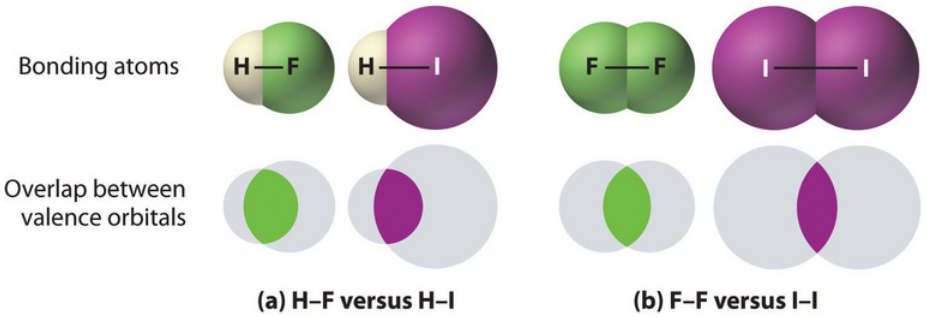


Figure 9.9.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) 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 8.6. 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.

> *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 9.9.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 9.9.1 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 9.9.2: Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

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

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the

bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{9.9.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_3(l) + 11\,O_2(g) \rightarrow 7\,CO_2(g) + 8\,H_2O(g) \tag{9.9.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Binds Broken (kJ/mol) and Bonds Formed (kJ/mol)

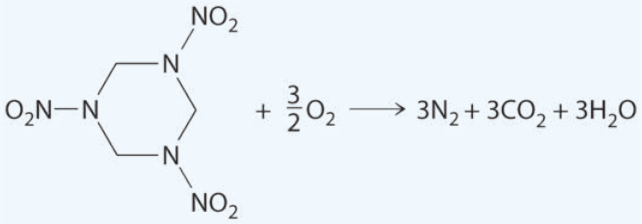
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7 kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 9.9.1: Explosives

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 9.9.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table 9.9.1.

Asked for: ΔH_{rxn} per mole

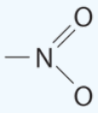
Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.

B. Use Equation 9.9.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($–NO_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

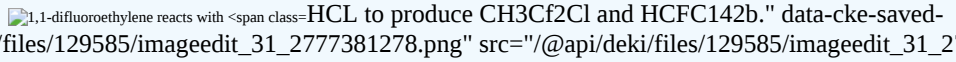
B From Equation $9.9.1$, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

? Exercise $9.9.1$: Freon

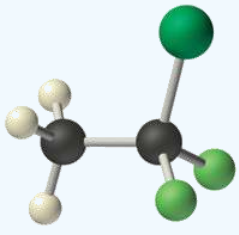
The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:



Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

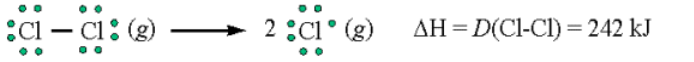
−54 kJ/mol



HCFC-142b

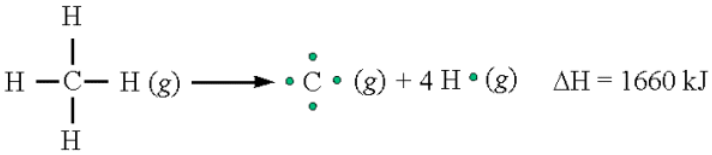
Bond Dissociation Energy

Bond Dissociation Energy (also referred to as Bond energy) is the enthalpy change (ΔH, heat input) required to break a bond (in 1 mole of a gaseous substance)



where "D(Cl-Cl)" represents the bond dissociation energy for the Cl-Cl bond

What about when we have a compound which is not a diatomic molecule? Consider the dissociation of ***methane***:



There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$D(C-H) = (1660/4)\, kJ/mol$$
$$= 415\, kJ/mol$$

> The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table 9.9.4: Average bond energies:

Bond	(kJ/mol)
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction.



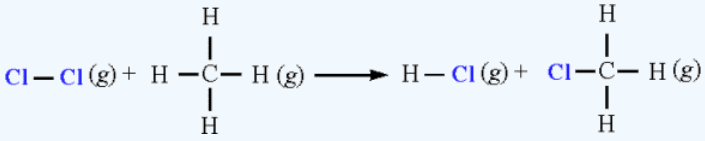
Bond Energies and the Enthalpy of Reactions

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we do not know the enthalpies of formation ((ΔH_f^o)for the reactants and products:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{9.9.3}$$

Example 9.9.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 9.9.3, which requires tabulating bonds broken and formed.

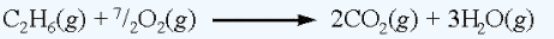
- **Bonds broken**: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed**: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

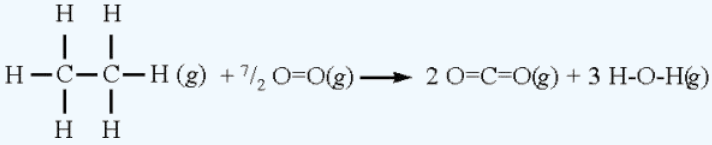
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)] \\ &= [242kJ+413kJ]-[431kJ+328kJ] \\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 9.9.3: Combustion of Ethane

What is the enthalpy of reaction for the combustion of 1 mol of ethane?





Solution

We use Equation 9.9.3, which requires tabulating bonds broken and formed.

- **bonds broken**: 6 moles C-H bonds, 1 mol C-C bonds, $^7/_2$ moles of O=O bonds

- **bonds formed**: 4 moles C=O bonds, 6 moles O-H bonds

$$\begin{aligned}\Delta H &= [(6\times 413)+(348)+(\frac{7}{2}\times 495)]-[(4\times 799)+(6\times 463)]\\ &= 4558-5974\\ &= -1416\ kJ\end{aligned}$$

Therefor the reaction is exothermic.

Table 9.9.5: Bond strength and bond length

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-C	348	1.54
C=C	614	1.34
C≡C	839	1.

As the number of bonds between two atoms increases, the bond grows shorter and stronger

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.

The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- Energy is always **released** to make bonds, which is why the enthalpy change for breaking bonds is always **positive**.
- Energy is always **required** to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is always **negative** because the system is releasing energy when forming bond.

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- **8.8: Strength of Covalent Bonds** is licensed CC BY-NC-SA 3.0.

CHAPTER OVERVIEW

10: Bonding II: Additional Aspects

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In this chapter, we begin with a general method for predicting the structures of simple covalent molecules and polyatomic ions; then we discuss the actual distribution of electrons in covalent bonds. We apply two distinct approaches for describing covalent bonds:

1. a localized model to describe bonding in molecules with two or more atoms attached to a central atom and
2. a delocalized model to explain and predict which diatomic species exist and which do not exist.

We conclude by describing more complex molecules and ions with multiple bonds. The tools you acquire in this chapter will enable you to explain why Ca_2 is too unstable to exist in nature and why the unpaired electrons on O_2 are crucial to the existence of life as we know it. You will also discover why carbon, the basic component of all organic compounds, forms four bonds despite having only two unpaired electrons in its valence electron configuration and how the structure of retinal, the key light-sensing component in our eyes, allows us to detect visible light.

Topic hierarchy

10.1: Bonding Theories
10.2: Introduction to Valence Bond Theory
10.3: Hybridization of Atomic Orbitals
10.4: Multiple Covalent Bonds
10.5: Molecular Orbital Theory
10.6: Exercises

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10.1: Bonding Theories

As we have talked about using Lewis structures to depict the bonding in organic compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

In this chapter, the **valence bond theory** is introduced to describe bonding in organic molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Valence bond theory is adequate for describing many aspects of organic structure. In some cases, however, chemists need to use a different model, called **molecular orbital (MO) theory**, to talk about covalent bonds in which electrons are shared not just between two atoms, but between several, or even over an entire molecule.

Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals.

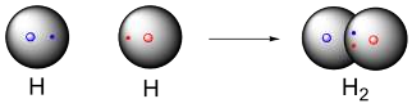


Figure 10.1.1: Addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

These two electrons are now attracted to the positive charge of *both* of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second.

But something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.

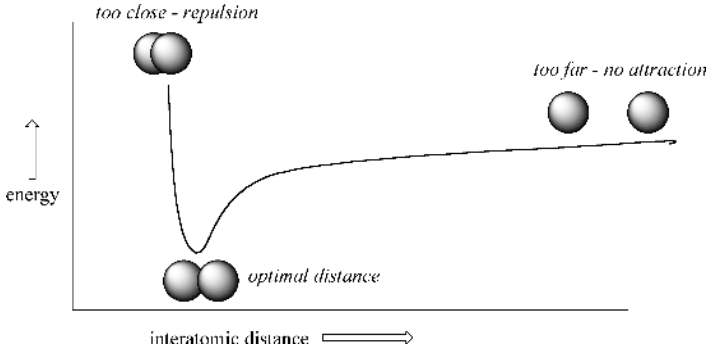


Figure 10.1.2.: Potential of interaction for the addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the

optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

It is not accurate, however, to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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10.2: Introduction to Valence Bond Theory

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

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. 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. 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.

Valence Bond Theory: A Localized Bonding Approach

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule*. Possibly unaware that Lewis's model existed, Walter Heitler and Fritz London came up with the idea that resonance and wavefunctions contributed to chemical bonds, in which they used dihydrogen as an example. Their theory was equivalent to Lewis's theory, with the difference of quantum mechanics being developed. Nonetheless, Heitler and London's theory proved to be successful, providing Linus Pauling and John C. Slater with an opportunity to assemble a general chemical theory containing all of these ideas. Valence Bond Theory was the result, which included the ideas of resonance, covalent-ionic superposition, atomic orbital overlap, and hybridization to describe chemical bonds.

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. 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 10.2.1).

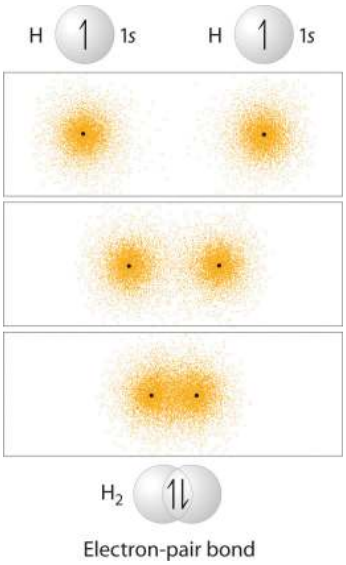


Figure 10.2.1: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray 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 both Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, 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 10.2.2 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.

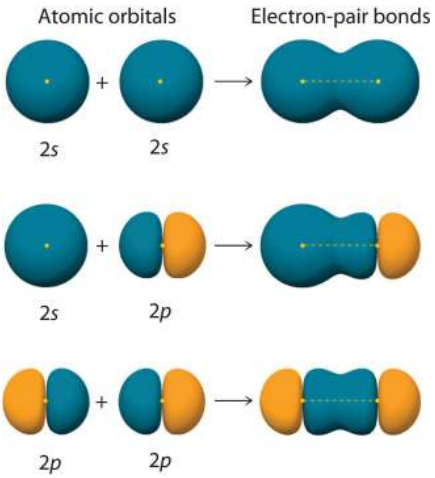


Figure 10.2.2: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Note

An important aspect of Valence Bond theory is the concept of maximum overlap to form the strongest possible covalent bonds.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. 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:



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.

Reliability of Valence Bond Theory and Uses

As one can see, Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen's paramagnitism; it predicts that oxygen is diamagnetic. A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used. In reality, that is not the case. Also, sp^2d and sp^3 both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or the other shape (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape.

Contributors and Attributions

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10.3: Hybridization of Atomic Orbitals

Learning Objectives

- To describe the hybridication in the bonding of simple compounds via valence bond theory.

The localized **valence bonding theory** uses a process called hybridization, 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 orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

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 10.3.0

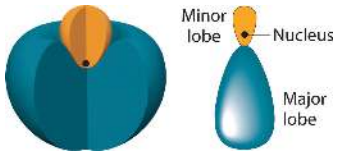


Figure 10.3.0: The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure 10.3.1 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 11.3.1, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{10.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{10.3.2}$$

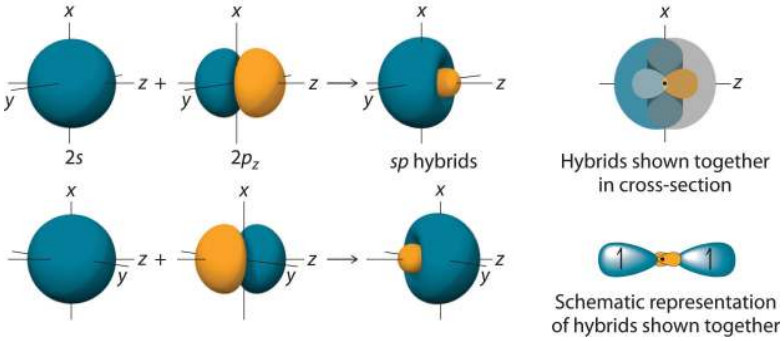


Figure 10.3.1: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

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:

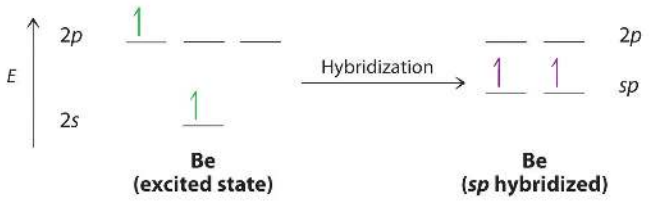


Figure 10.3.2, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

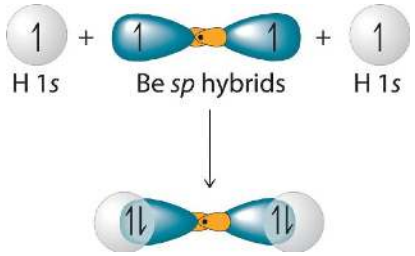


Figure 10.3.2: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule 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 10.3.3). 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.

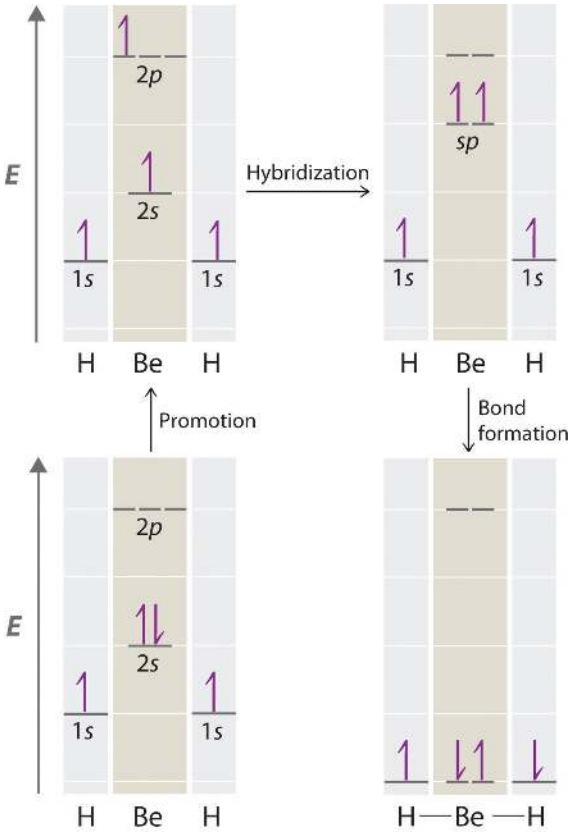


Figure 10.3.3: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom 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.

https://chem.libretexts.org/@go/page/37044

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, as predicted by the Lewis and VSEPR approaches. 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:

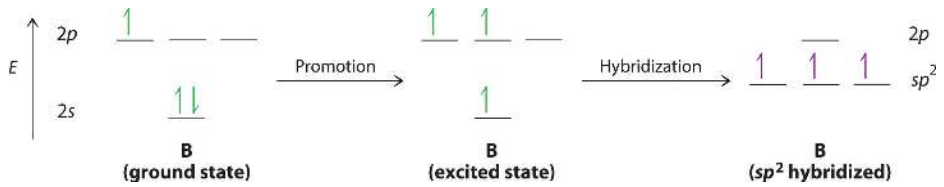


Figure 10.3.4). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

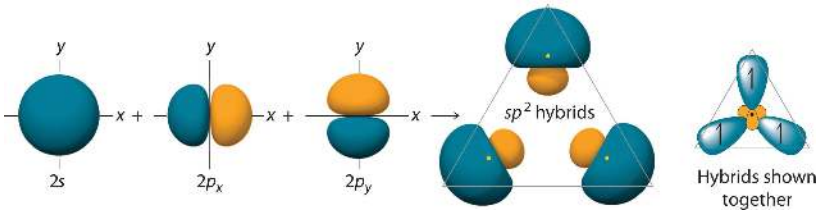
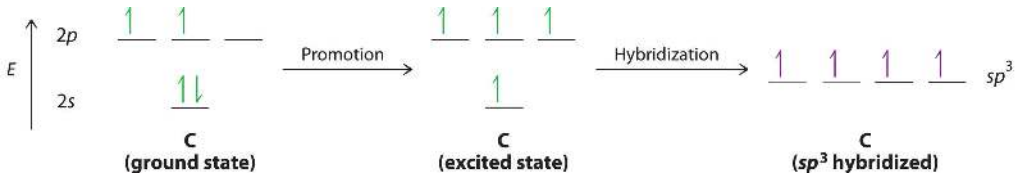


Figure 10.3.4: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^2 2p^2$ 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 10.3.5). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

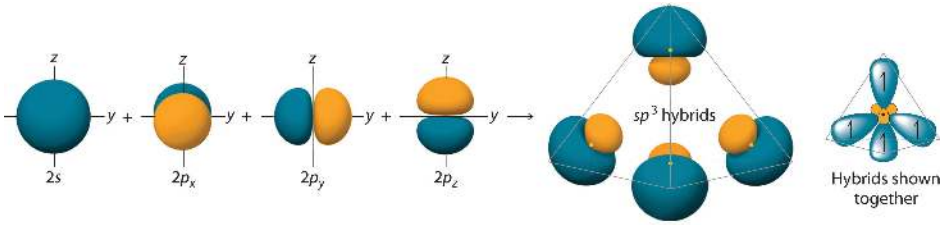
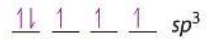


Figure 10.3.5: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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.

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 $2s^2 2p^3$ 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.



Valence Bond Method & sp3 Hybridization: https://youtu.be/2hxKLGWQ5EQ

Example 10.3.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VPSER approach to 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 10.3.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer

a. 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.
b. 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.

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 that point toward the vertices of a trigonal bipyramid (part (a) in Figure 10.3.6). 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 oriented toward the vertices of an octahedron (part (b) in Figure 10.3.6). 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.

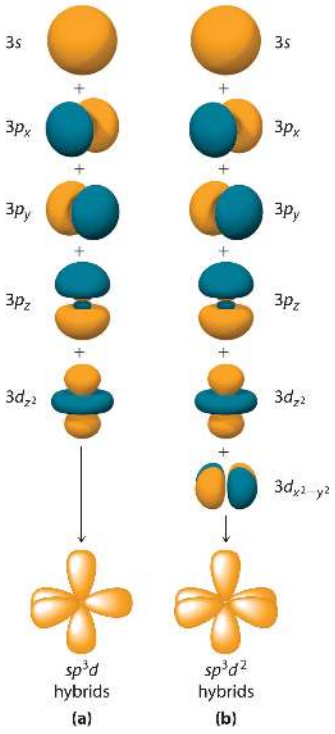


Figure 10.3.6: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 10.3.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. SO_4^{2-}
c. 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:

a. **A** Using the VSEPR model, we find that 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.
b. **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.
c. **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 10.3.2

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+
b. BrF_3
c. SiF_6^{2-}

Answer

a. sp^3 with four P–Cl bonds
b. sp^3d with three Br–F bonds and two lone pairs
c. 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 10.3.3: OF_4

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 The VSEPR model predicts that 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 10.3.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer sp^3d^2 hybridization; no



Expanded Octet Hybridization: https://youtu.be/1WpxXcKl_Io

Summary

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

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.

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10.4: Multiple Covalent Bonds

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.

Non-singular Bonding

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 10.4.1). The sp^2 hybridization can be represented as follows:

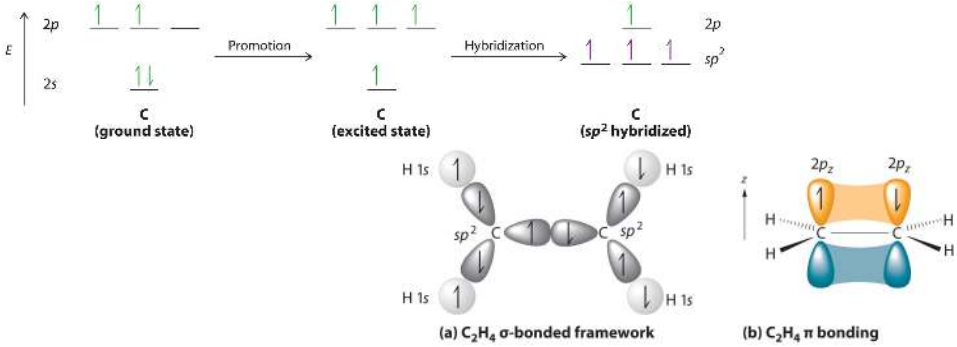


Figure 10.4.1: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four 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 10.4.1). 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 10.4.2. 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.

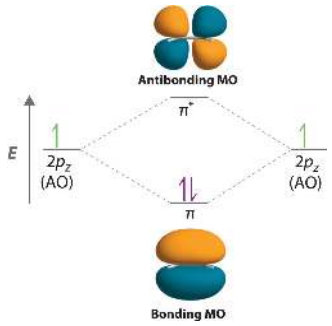


Figure 10.4.2: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.



sp2 Hybridization: https://youtu.be/EepTvePnfBA

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 10.4.3).

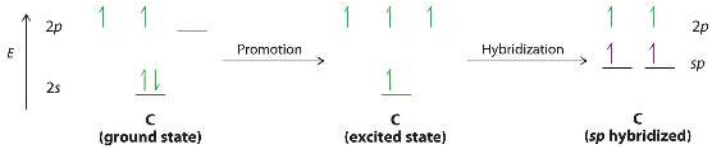


Figure 10.4.3). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular 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.

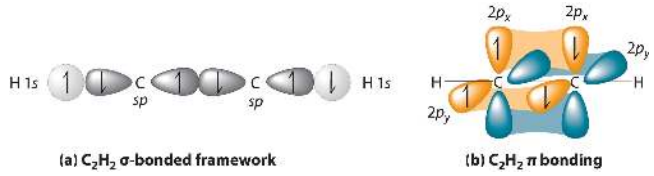


***Figure* 10.4.3:** *Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.*

Note

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 10.4.1

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

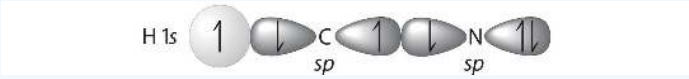
Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

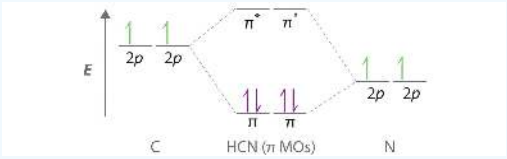
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized p orbitals 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 2p atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2p 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 2p 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.



sp Hybridization: https://youtu.be/epQXzG9WDRw

Summary

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

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.

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10.5: Molecular Orbital Theory

Learning Objectives

- To use molecular orbital theory to predict bond order
- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

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.

Previously, 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 is a *delocalized* approach to bonding.

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 discussed previously, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. 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*:

$$\begin{aligned} MO(1) = \quad & AO(atom\ A) \quad + \quad AO(atom B) \\ MO(1) = \quad & AO(atom\ A) \quad - \quad AO(atom B) \end{aligned} \tag{10.5.1}$$

The molecular orbitals created from Equation 10.5.1 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 σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 10.5.1). 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.

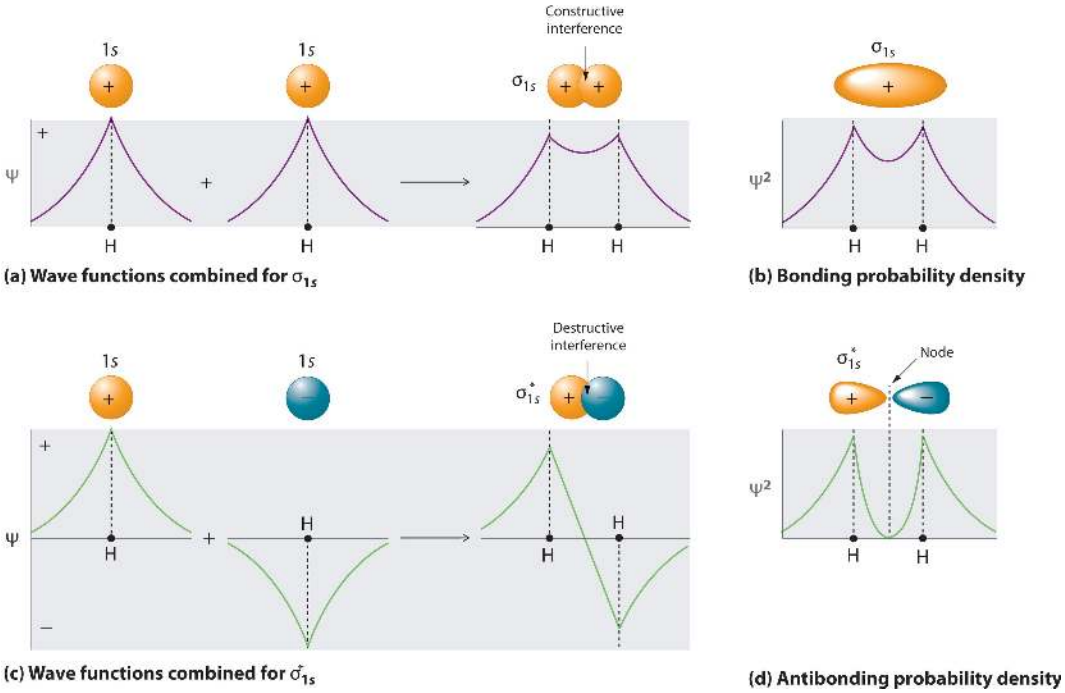


Figure 10.5.1: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{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 (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{10.5.2}$$

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 10.5.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{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:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{10.5.3}$$

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

The electron density in the σ_{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 σ_{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 $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ 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 destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^\star_{1s}$ 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 $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^{\star}_{1s}$ (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 10.5.2

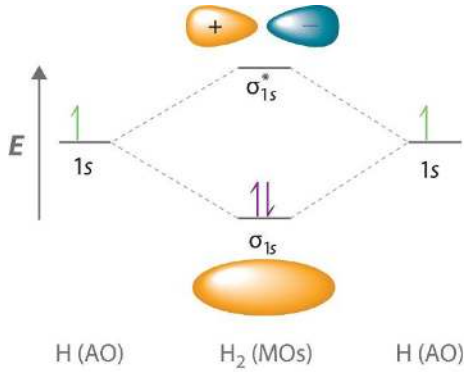


Figure 10.5.2: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *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).*

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 10.5.2). 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 σ_{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, 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:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{10.5.4}$$

To calculate the bond order of H_2, we see from Figure 10.5.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{10.5.5}$$

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 10.5.2 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.

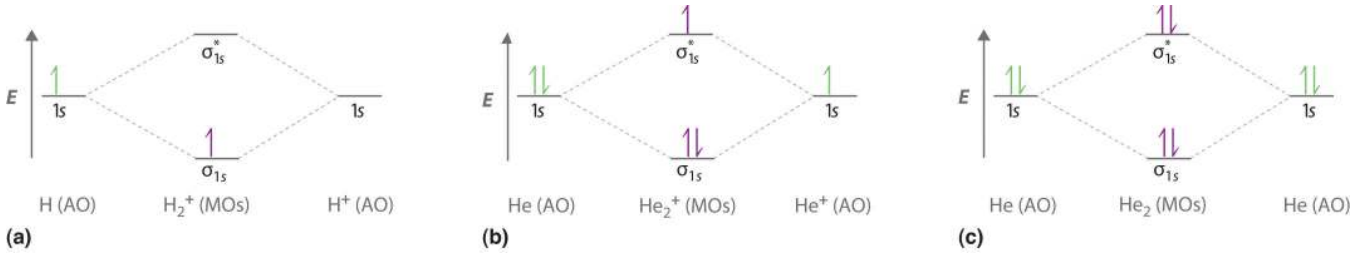


Figure 10.5.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure 10.5.3 shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{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 10.5.1, these predictions agree with the experimental data.

Part (b) in Figure 10.5.3 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 σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma_{1s}^\star$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ 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 10.5.1).

Table 10.5.1: 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^+	$(\sigma_{1s})^2(\sigma_{1s}^\star)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^\star)^2$	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 10.5.3 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^\star$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ 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.



Molecular Orbital Theory: https://youtu.be/XgtOG0ezw78

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 10.5.1

Use a molecular orbital energy-level diagram, such as those in Figure 10.5.3, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

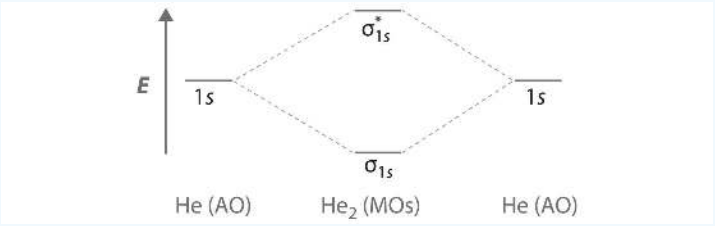
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

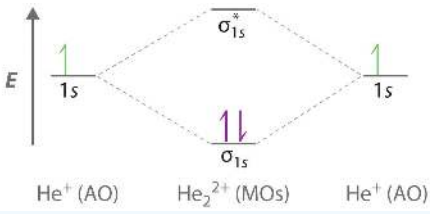
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning 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 σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma_{1s}^{\star}$ 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 (σ_{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 10.5.1

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 $(\sigma_{1s})^2(\sigma_{1s}^{\star})^2$ 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 10.5.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{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 σ_{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 10.5.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

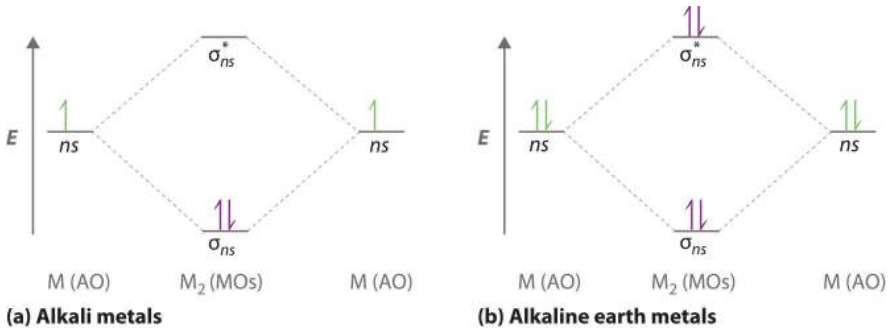


Figure 10.5.4: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{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 10.5.3

As shown in part (b) in Figure 10.5.4, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{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 10.5.2

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

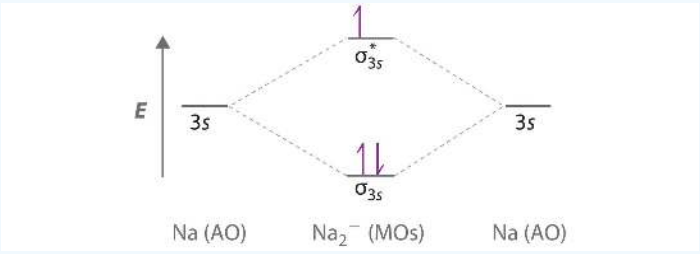
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

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 σ_{3s} molecular orbital, a half-filled σ_{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 10.5.2

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 that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{10.5.6}$$

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 10.5.5, 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 σ_{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):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{10.5.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{10.5.8}$$

In this combination, shown in part (b) in Figure 10.5.5, 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).

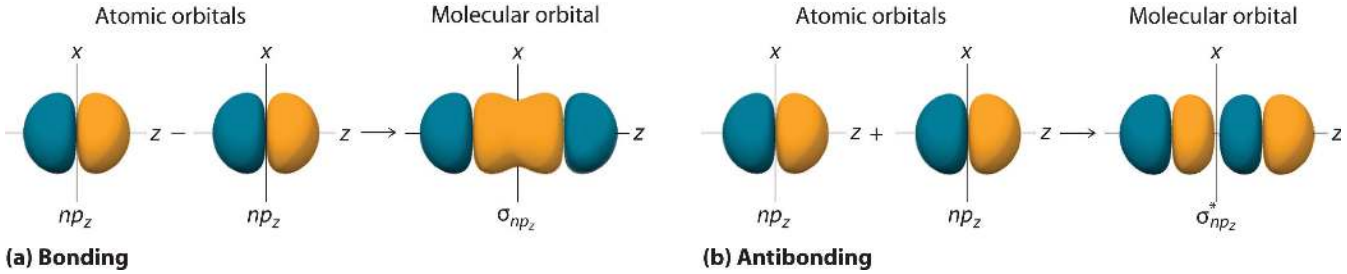


Figure 10.5.5: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms 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.

> 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 10.5.6, 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) orbital (a 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..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{10.5.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{10.5.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{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 π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

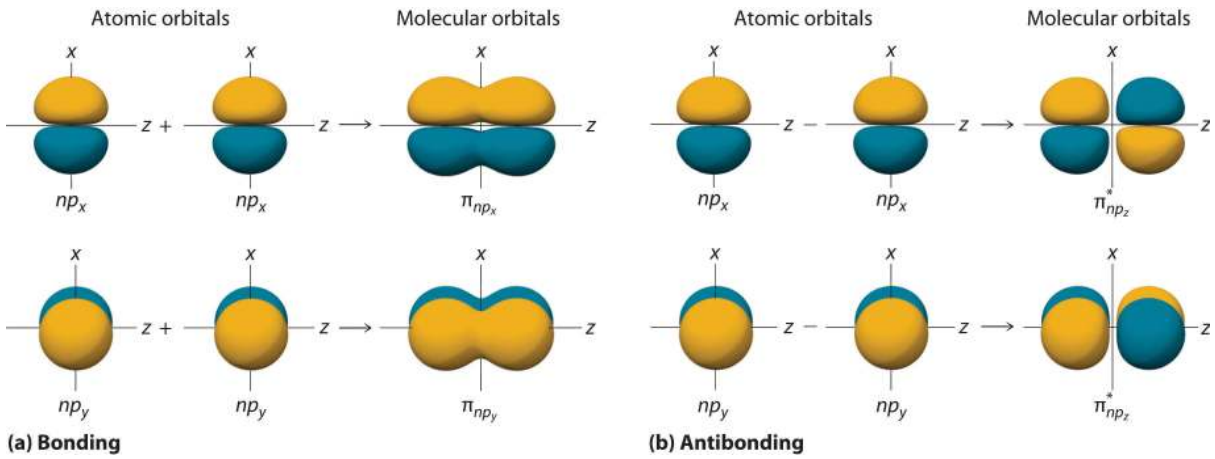


Figure 10.5.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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 10.5.7 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.

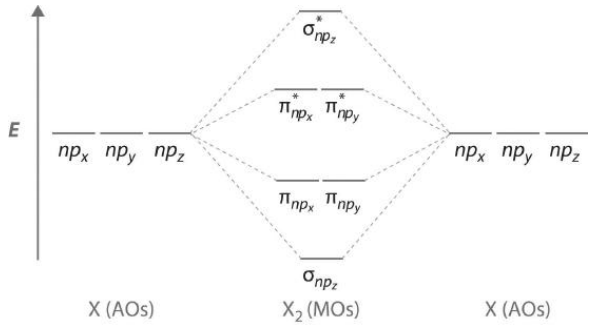


Figure 10.5.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals 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 10.5.8, 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.

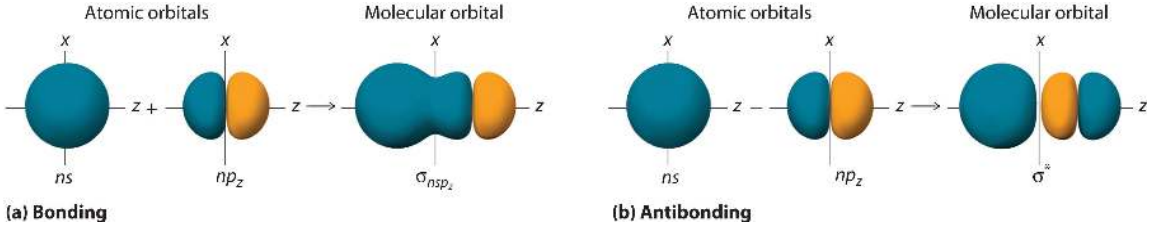


Figure 10.5.8: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

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Second Row Diatomic Molecules

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

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).
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.

> 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 10.5.9; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2p atomic orbitals because of the large difference in energy between the 2s and 2p atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2p orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{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 σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π* 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) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

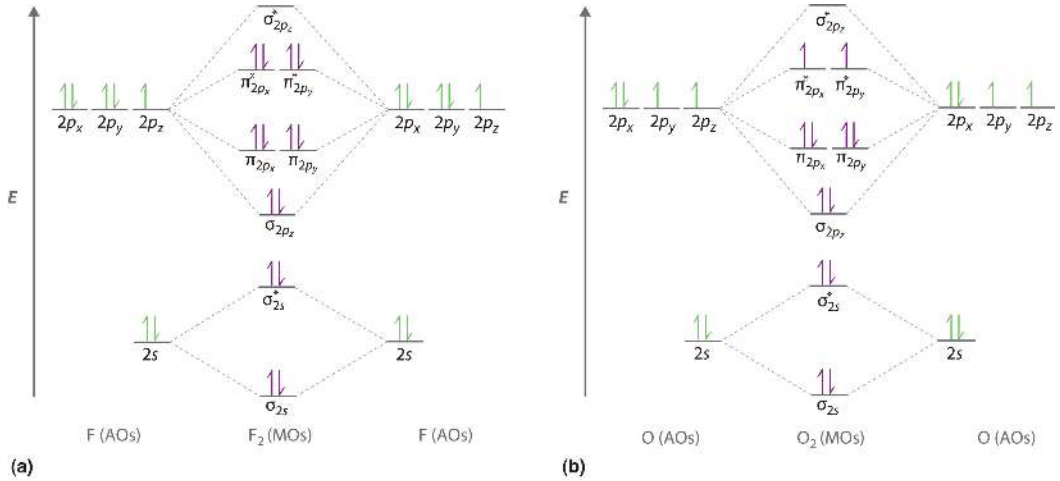


Figure 10.5.9: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^{\star}_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 $\left(\pi^{\star}_{np_z}, \pi^{\star}_{np_y}\right)$ 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.

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 10.5.9. 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 σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{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 π^* 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 (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

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 10.5.10, 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 10.5.10: 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. Full video can be found at https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

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 σ_{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 σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 10.5.11. Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 10.5.11). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

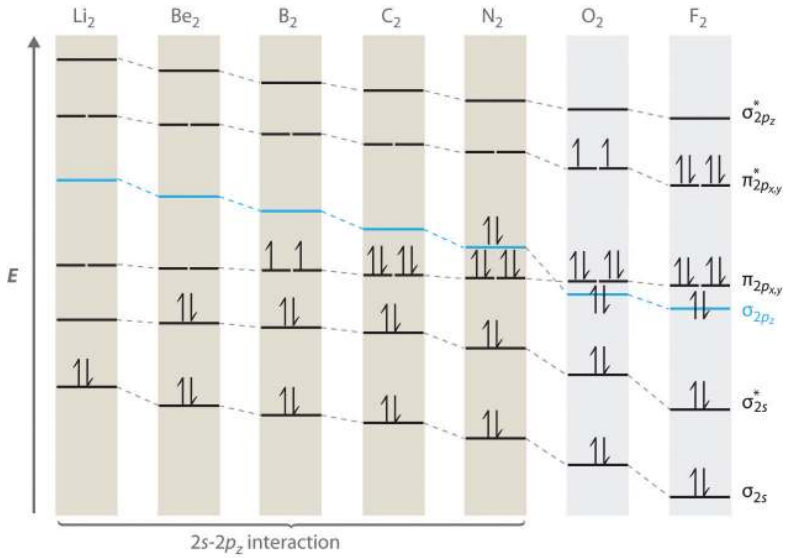


Figure 10.5.11: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{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 2*s* and 2*p* 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 10.5.3

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

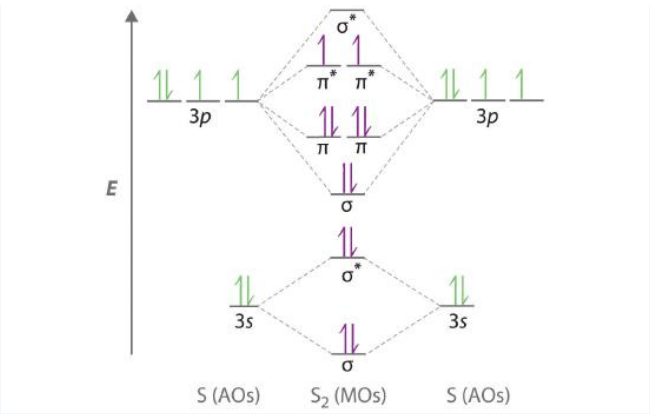
Strategy:

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 10.5.9 and Figure 10.5.11, 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 σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 10.5.11), the σ_{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 π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ 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 10.5.3

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

$(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^{\star}_{x,y}})^4$

bond order of 1;

no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. 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 10.5.12 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.

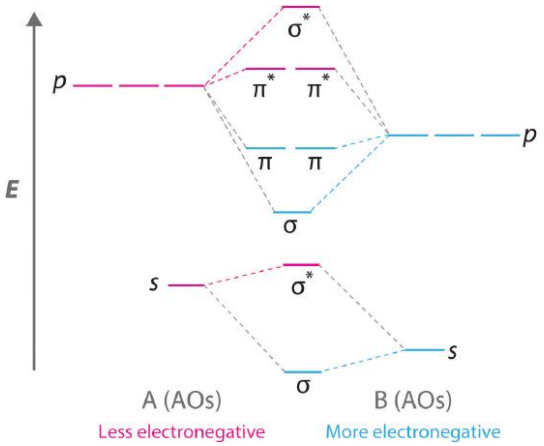


Figure 10.5.12: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *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 10.5.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 10.5.11). 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 π^* 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.

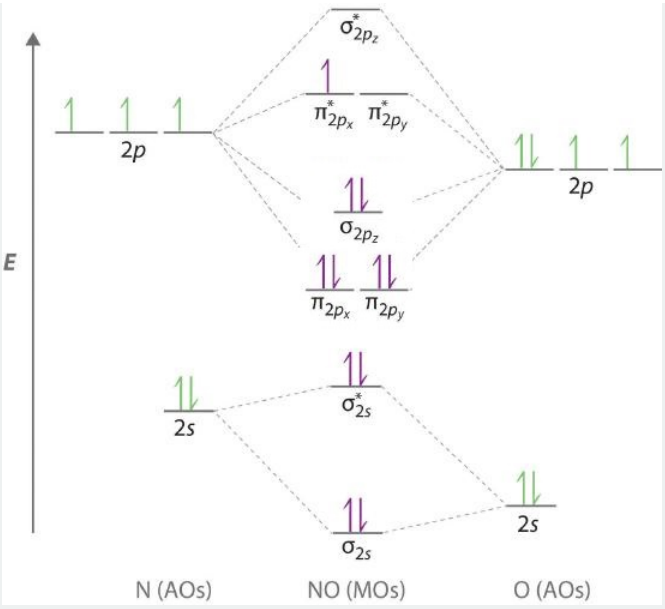


Figure 10.5.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\left(\sigma^{\star}_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi_{2p^{\star}_{x,y}}\right)^2$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 10.5.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 10.5.13, 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.



Molecular Orbital Bonding for Second Row Elements: https://youtu.be/A_5Xa3sK_YE

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 10.5.14 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 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 $H^{\delta+}--Cl^{\delta-}$.

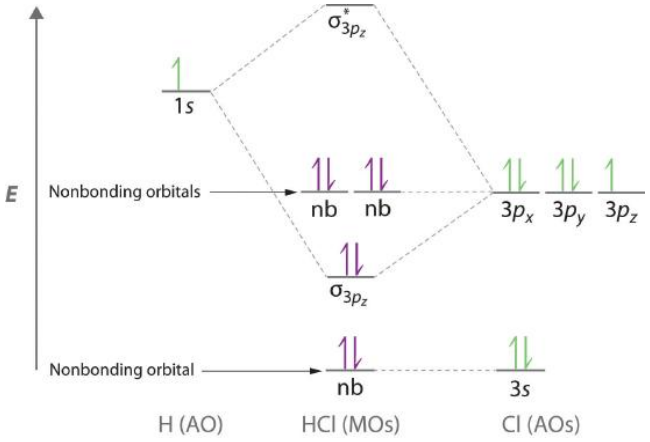


Figure 10.5.14: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have **no effect** on bond order.*

Example 10.5.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 10.5.12to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

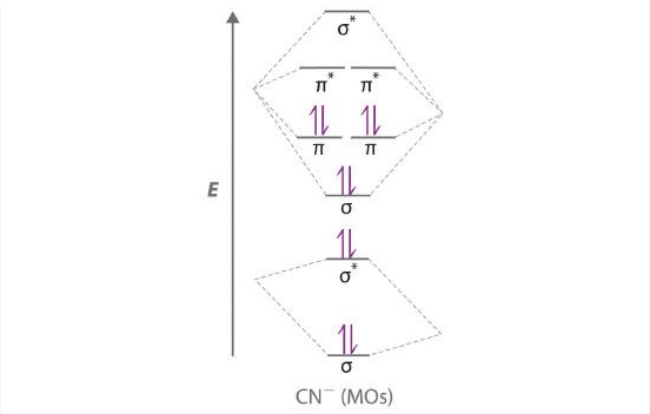
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 10.5.12in 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 10.5.12fills 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 10.5.4

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

- 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.

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.

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