CHEMISTRY 101A GENERAL COLLEGE CHEMISTRY



Torrey Glenn
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City College of San Francisco

Chemistry 101A General College Chemistry

Torrey Glenn

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Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

Course Objectives

After successful completion of this course, students will be able to:

- Outcome 1: Predict and write balanced net ionic equations for acid-base and precipitation reactions.
- Outcome 2: Analyze and solve stoichiometry problems including limiting reactants, elemental analyses, and material balances in aqueous solution.
- Outcome 3: Solve classical gas law problems and interpret the behavior of gases using the kinetic theory, and predict circumstances under which non-ideal behavior becomes important.
- Outcome 4: Derive energies and enthalpies of physical and chemical processes from calorimetric data, and solve problems involving enthalpies of formation and Hess' law.
- Outcome 5: Derive and use classical and modern relationships for electromagnetic radiation.
- Outcome 6: Interpret electron density and probability plots for hydrogen-like orbitals, interpret atomic emission spectra to atomic energy levels, apply the quantum theory to polyelectronic atoms, and relate electron configurations to atomic properties.
- Outcome 7: Predict, for given molecules or polyatomic ions: 1. orbital hybridization and orbital geometry 2. molecular geometry 3. types and numbers of covalent bonds in molecules 4. bond length, bond angles, and bond energies 5. polarity, resonance, and formal charges
- Outcome 8: Use molecular orbital energy diagrams for diatomic molecules to determine bond order and magnetic properties of a molecule.
- Outcome 9: Solve initial-value equilibrium problems including weak acid dissociation, interpret equilibrium constants, and use Le Chatelier's principle to predict the effect of a disturbance on an equilibrium system.
- Outcome 10: Correlate physical properties of solid substances with interparticle attractions.
- Outcome 11: Construct and interpret a Born-Haber cycle.
- Outcome 12: Describe and use laboratory techniques, including proper recording of laboratory data, the proper use of weighing balances, spectrophotometers, and other equipment, the proper disposal of chemical waste, and safety procedures and precautions.

City College of San Francisco: Chemistry 101A

General College Chemistry

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SECTION OVERVIEW

Topic A- Equations, Formulas, and Stoichiometry

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

1. Write and balance chemical equations involving pure elements and compounds.
2. Find empirical and molecular formulas and molar masses of compounds from analytical data, and use molecular formulas to determine percent composition.
3. Use combustion analysis to determine the empirical formula of an organic compound.
4. Use stoichiometric relationships to determine limiting reactants, masses of reactants and products, and percent yield, given appropriate data.
5. Determine the composition of a mixture of substances, given appropriate analytical data.
6. Know the names and formulas of common inorganic compounds.

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CHAPTER OVERVIEW

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SECTION OVERVIEW

0.1: What should I know already?

Many students mistakenly believe that Chem 101A is an introductory course, one that can be taken without having taken any chemistry courses in the past. This is not the case! At a minimum, you should be familiar with the following information already. "Familiar" means that you should be able to answer questions about these topics with a minimum of review (no more than 10 minutes for any one topic). Do not expect to be able to spend time reviewing these basic concepts during Chem 101A: we will expect you to know, and use, this material from the very beginning of the course.

- The basic structure of the atom (protons/neutrons/electrons, how many, where they are).
- What a mole is, how to interconvert grams and moles, and the significance of Avogadro's number.
- How to recognize whether a chemical equation is balanced, and how to balance a simple chemical equation.
- How to deal with molarity (using any two of the mass of solute, the volume of solution, and the molarity to calculate the third).
- How to use a balanced equation to interrelate masses and numbers of moles of the chemicals in the reaction. A typical example: "if you use 5 moles (or 5 grams) of chemical X, how many moles (or grams) of chemical Y will you make?"
- The difference between an ionic and a covalent bond, and the manner in which each type of bond is formed.
- How to write the formula of an ionic compound, if you know the formulas and charges on the constituent ions (for instance, "what is the formula of ammonium sulfide, given that ammonium ion is NH_4^+ and sulfide ion is S^{2-}?")

You should also know the names and symbols for common elements and ions. A representative list is on the back of this sheet. You need not know ALL of these, but you should know MOST of them. (We are also assuming that you are familiar with the significant figure rules for arithmetic calculations, although you can learn/review these during the early part of the semester.) This topics are covered in the Foundations text for those who wish to review.

If you have not learned one or more of the above topics, you should seriously consider enrolling in Chem 40, even if you qualified for Chem 101A based on the placement test. "Passing" the placement test does NOT mean that you will pass Chem 101A. We set the placement test cutoff at the point where students who scored below the cutoff were guaranteed to fail Chem 101A: the test only screens out those students who have no realistic chance of passing the course.

If you know more chemistry than this, good for you! The more you already know, the easier you will find Chem 101A. We will cover topics such as gas laws, heats of reaction, atomic orbitals, Lewis dot structures, and so forth in detail in Chem 101A, but these are also covered in most introductory courses (including our Chem 40), and prior knowledge of them is very helpful.

COMMON ELEMENTS AND IONS

(arranged in order of increasing atomic number)

Symbol	Name	Charge on ion	Name of ion
H	hydrogen	+1	hydrogen
He	helium	none	
C	carbon	none	
N	nitrogen	-3	nitride
O	oxygen	-2	oxide
F	fluorine	-1	fluoride
Na	sodium	+1	sodium
Mg	magnesium	+2	magnesium
Al	aluminum*	+3	aluminum*
Si	silicon	none	
P	phosphorus	-3	phosphide
S	sulfur**	-2	sulfide**
Cl	chlorine	-1	chloride
K	potassium	+1	potassium
Ca	calcium	+2	calcium
Fe	iron	(more than one)	
Cu	copper	(more than one)	
Zn	zinc	+2	zinc
Br	bromine	-1	bromide
Ag	silver	+1	silver
Sn	tin	(more than one)	
I	iodine	-1	iodide
Au	gold	(more than one)	
Hg	mercury	(more than one)	
Pb	lead	(more than one)	

Note: we do not expect you to know the ion charges on those elements that can form more than one ion (Fe, Cu, Sn, etc.).

*This name is spelled “aluminium” in many English-speaking countries.

**These names are spelled “sulphur” and “sulphide” in many English-speaking countries.

A few common polyatomic ions that you should know

Formula	Name
OH^-	hydroxide
NH_4^+	ammonium
CO_3^{2-}	carbonate
NO_3^-	nitrate
PO_4^{3-}	phosphate
SO_4^{2-}	sulfate
HCO_3^-	bicarbonate (common name) hydrogen carbonate (official name)

Diatomic Molecules

Most elements in their pure form exist as **individual atoms**. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called **diatomic molecules.** You should be familiar with these. The elements that exist as diatomic molecules are hydrogen (H_2), nitrogen (N_2), fluorine (F_2), oxygen (O_2), iodine (I_2), chlorine (Cl_2) and bromine (Br_2).

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SECTION OVERVIEW

0.2: Essential Ideas of Chemistry

Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you will learn many of the essential principles underlying the chemistry of modern-day life.

9.2.1: Chemistry in Context

9.2.2: Phases and Classification of Matter

9.2.3: Physical and Chemical Properties

9.2.4: Measurements

9.2.5: Measurement Uncertainty, Accuracy, and Precision

9.2.6: Mathematical Treatment of Measurement Results

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9.2.1: Chemistry in Context

Learning Objectives

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys—for example, copper and tin were mixed together to make bronze—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations were spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform “base metals” such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life (Figure **9.2.1.1**).



Figure **9.2.1.1**: This portrayal shows an alchemist’s workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation).

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter. This effort has been so successful that many people do not realize either the central position of chemistry among the sciences or the importance and universality of chemistry in daily life.

Chemistry: The Central Science

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields (Figure **9.2.1.2**). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world’s population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

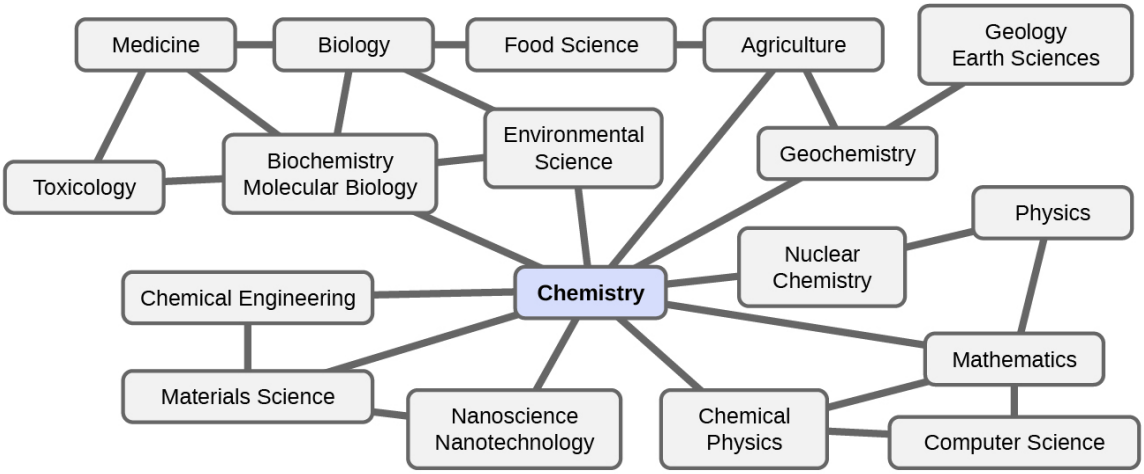


Figure **9.2.1.2**: Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes and how they occurred, their causes, the changes in energy that accompany them, and the principles and laws involved. As you learn about these things, you will be learning chemistry, the study of the composition, properties, and interactions of matter. The practice of chemistry is not limited to chemistry books or laboratories: It happens whenever someone is involved in changes in matter or in conditions that may lead to such changes.

The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve a hypothesis, a tentative explanation of observations that acts as a guide for gathering and checking information. We test a hypothesis by experimentation, calculation, and/or comparison with the experiments of others and then refine it as needed.

Some hypotheses are attempts to explain the behavior that is summarized in laws. The laws of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific theories are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory

explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the scientific method (Figure **9.2.1.3**).

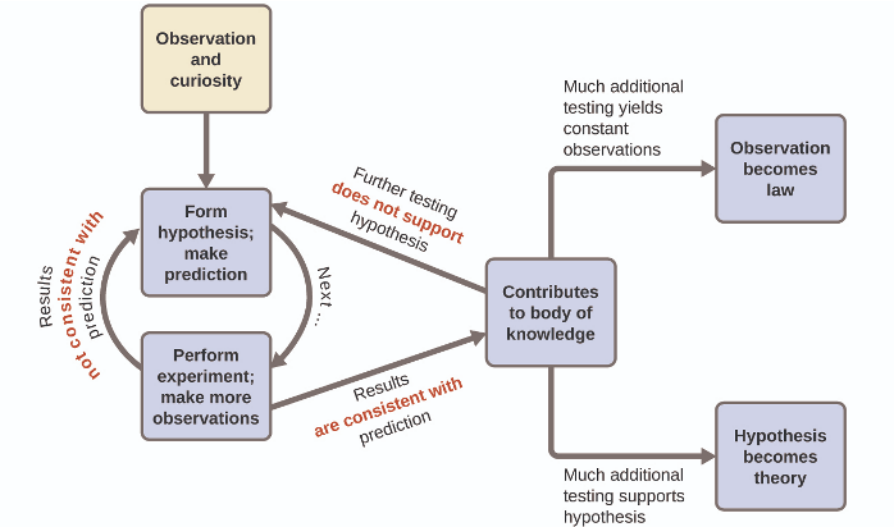


Figure **9.2.1.3**: The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behavior.

Macro is a Greek word that means “large.” The macroscopic domain is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes everyday and laboratory chemistry, where we observe and measure physical and chemical properties, or changes such as density, solubility, and flammability.

The microscopic domain of chemistry is almost always visited in the imagination. *Micro* also comes from Greek and means “small.” Some aspects of the microscopic domains are visible through a microscope, such as a magnified image of graphite or bacteria. Viruses, for instance, are too small to be seen with the naked eye, but when we’re suffering from a cold, we’re reminded of how real they are.

However, most of the subjects in the microscopic domain of chemistry—such as atoms and molecules—are too small to be seen even with standard microscopes and often must be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see. This domain includes the individual metal atoms in a wire, the ions that compose a salt crystal, the changes in individual molecules that result in a color change, the conversion of nutrient molecules into tissue and energy, and the evolution of heat as bonds that hold atoms together are created.

The symbolic domain contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs and drawings. We can also consider calculations as part of the symbolic domain. These symbols play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures (Figure 1.1.4) are macroscopic observations. But some properties of water fall into the microscopic domain—what we cannot observe with

the naked eye. The description of water as comprised of two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.

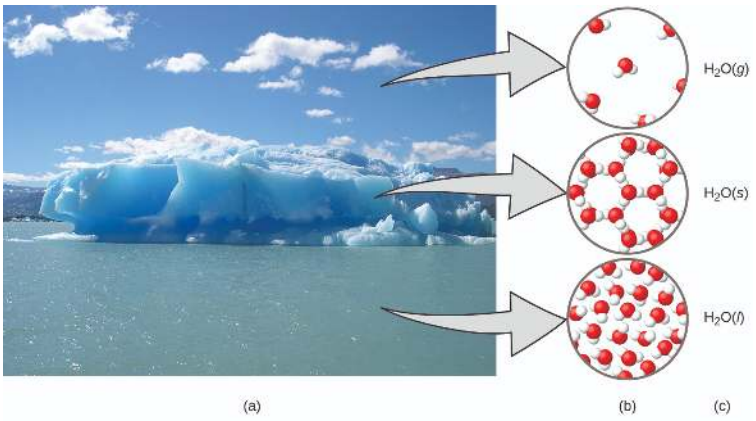


Figure **9.2.1.4**: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons).

Key Concepts and Summary

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behavior of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

Glossary

chemistry
study of the composition, properties, and interactions of matter

hypothesis
tentative explanation of observations that acts as a guide for gathering and checking information

law
statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

macroscopic domain
realm of everyday things that are large enough to sense directly by human sight and touch

microscopic domain
realm of things that are much too small to be sensed directly

scientific method
path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

symbolic domain

specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

theory

well-substantiated, comprehensive, testable explanation of a particular aspect of nature

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9.2.2: Phases and Classification of Matter

Learning Objectives

- Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Define and give examples of atoms and molecules
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- Distinguish between mass and weight
- Apply the law of conservation of matter

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure **9.2.2.1**). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A gas takes both the shape and volume of its container.

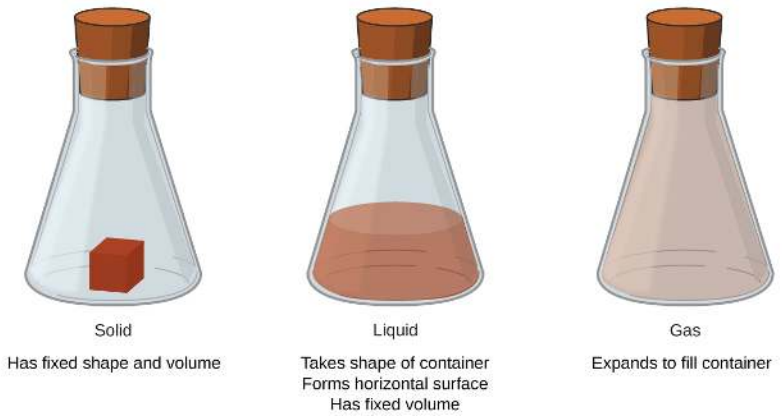


Figure **9.2.2.1**: The three most common states or phases of matter are solid, liquid, and gas.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A plasma is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure **9.2.2.2**). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.



Figure **9.2.2.2**: A plasma torch can be used to cut metal. (credit: “Hypertherm”/Wikimedia Commons)



Video 9.2.2.1*: In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this video to learn more about plasma and the places you encounter it.*

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The mass of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. Weight refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

The law of conservation of matter summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure **9.2.2.4**). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

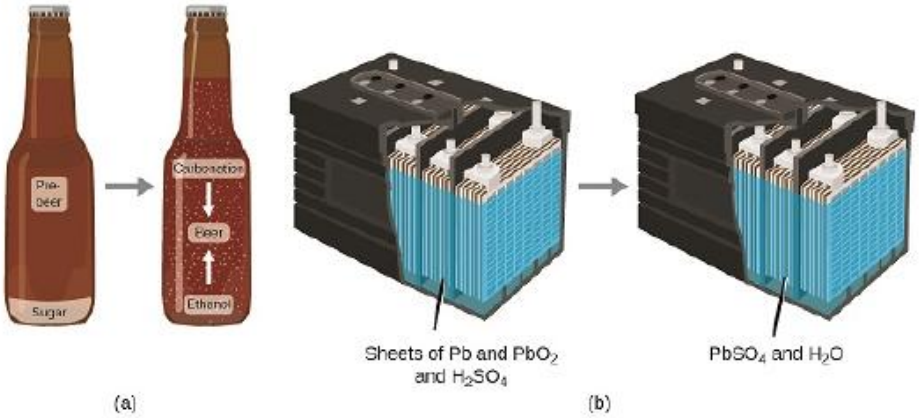


Figure 9.2.2.3: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

Atoms and Molecules

An atom is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) (Figure 1.2.4). This atom would no longer be gold if it were divided any further.

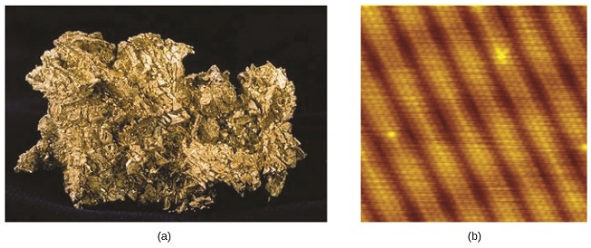


Figure 9.2.2.4: (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry. Other aspects of Dalton’s atomic theory are still used but with minor revisions (details of Dalton’s theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which

would require about 150 million carbon atom “dimes” to cover it. (Figure 9.2.2.5) shows increasingly close microscopic and atomic-level views of ordinary cotton.

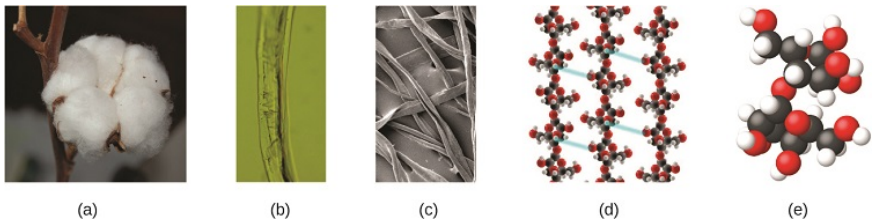


Figure 9.2.2.5: These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by “Featheredtar”/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world’s most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure 9.2.2.6). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A molecule consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.

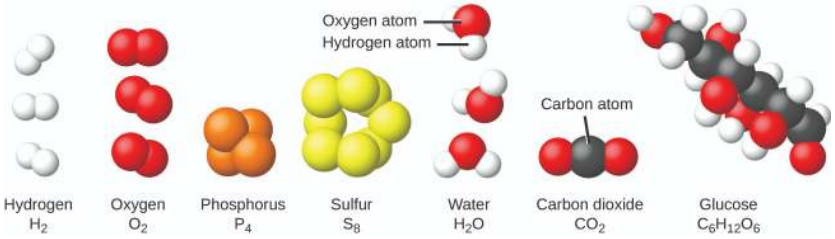


Figure 9.2.2.6: The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

Classifying Matter

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A pure substance has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called elements. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called compounds. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen (Figure 9.2.2.7). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—

this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).

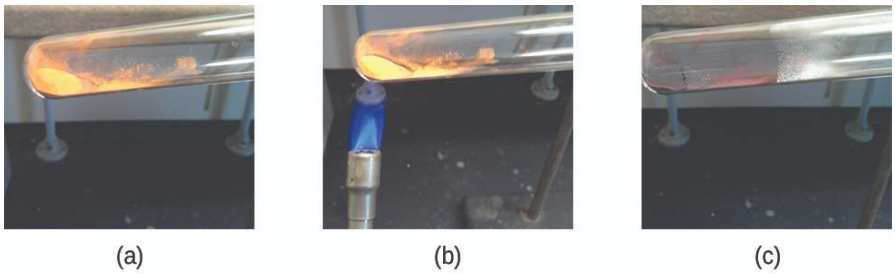


Figure 9.2.2.7: (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A mixture is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a heterogeneous mixture. Italian dressing is an example of a heterogeneous mixture (Figure **9.2.2.1*a***). Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A homogeneous mixture, also called a solution, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure **9.2.2.1*b***). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



Figure **9.2.2.7**: (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in (Figure 1.2.8).

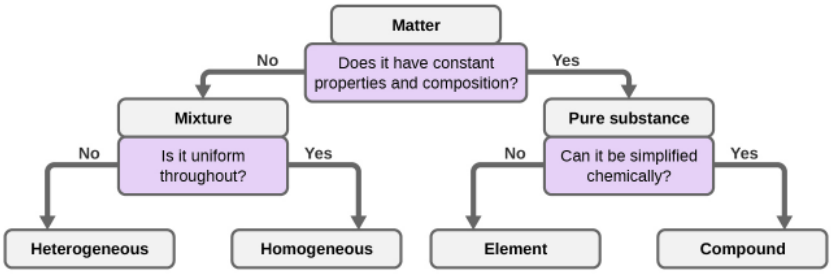


Figure **9.2.2.8**: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere (Table **9.2.2.1**). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Table **9.2.2.1**: Elemental Composition of Earth

Element	Symbol	Percent Mass	Element	Symbol	Percent Mass
oxygen	O	49.20	chlorine	Cl	0.19
silicon	Si	25.67	phosphorus	P	0.11
aluminum	Al	7.50	manganese	Mn	0.09
iron	Fe	4.71	carbon	C	0.08
calcium	Ca	3.39	sulfur	S	0.06
sodium	Na	2.63	barium	Ba	0.04
potassium	K	2.40	nitrogen	N	0.03
magnesium	Mg	1.93	fluorine	F	0.03
hydrogen	H	0.87	strontium	Sr	0.02
titanium	Ti	0.58	all others	-	0.47

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure **9.2.2.9**).

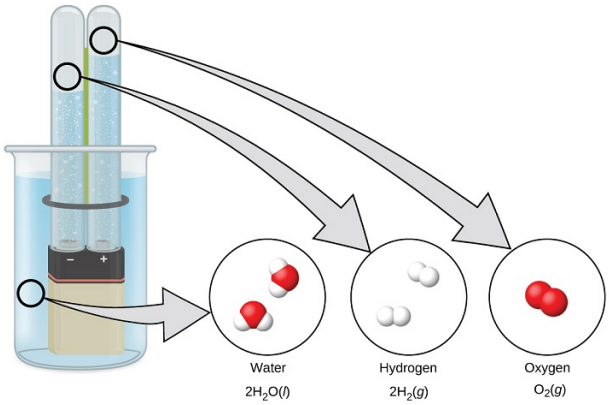


Figure **9.2.2.9**: The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure **9.2.2.10**). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

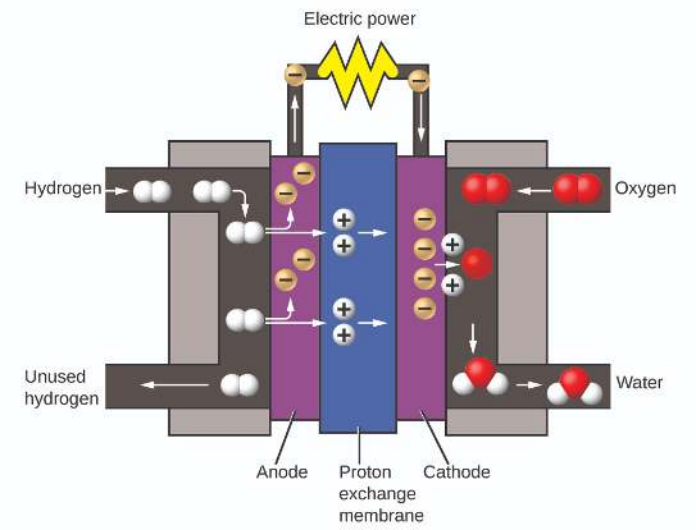


Figure **9.2.2.10**: A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure **9.2.2.11**) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Figure 9.2.2.11: Almost one-third of naturally occurring elements are used to make a modern cell phone. (credit: modification of work by John Taylor)

Contributors and Attributions

Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Glossary

atom
: smallest particle of an element that can enter into a chemical combination

compound
: pure substance that can be decomposed into two or more elements

element
: substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas
: state in which matter has neither definite volume nor shape

heterogeneous mixture
: combination of substances with a composition that varies from point to point

homogeneous mixture
: (also, solution) combination of substances with a composition that is uniform throughout

liquid
: state of matter that has a definite volume but indefinite shape

law of conservation of matter
: when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass
fundamental property indicating amount of matter

matter
anything that occupies space and has mass

mixture
matter that can be separated into its components by physical means

molecule
bonded collection of two or more atoms of the same or different elements

plasma
gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance
homogeneous substance that has a constant composition

solid
state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight
force that gravity exerts on an object

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9.2.3: Physical and Chemical Properties

Learning Objectives

- Identify properties of and changes in matter as physical or chemical
- Identify properties of matter as extensive or intensive

The characteristics that enable us to distinguish one substance from another are called properties. A physical property is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A physical change is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure **9.2.3.1**). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.



Figure **9.2.3.1**: (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr).

The change of one type of matter into another type (or the inability to change) is a chemical property. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure **9.2.3.2**). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



Figure **9.2.3.2**: (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include

reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure **9.2.3.3**).

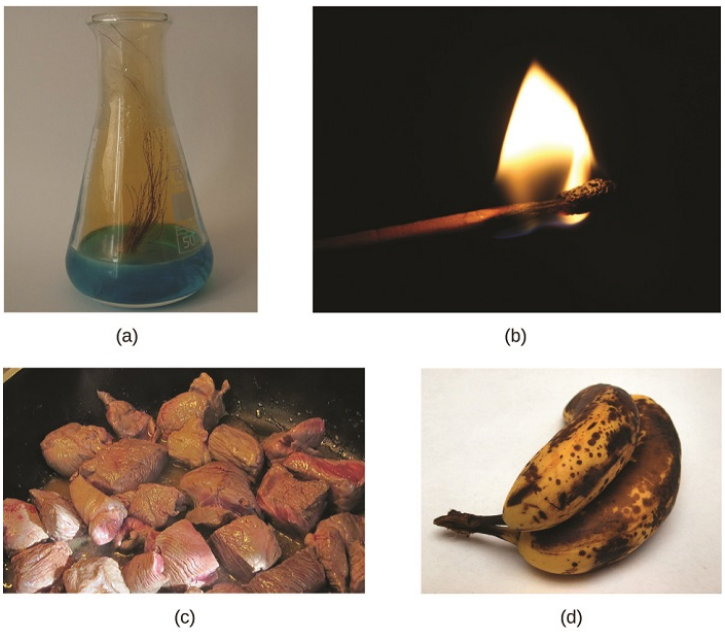


Figure **9.2.3.3**: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an extensive property. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an intensive property. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

Hazard Diamond

You may have seen the symbol shown in Figure **9.2.3.4** on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

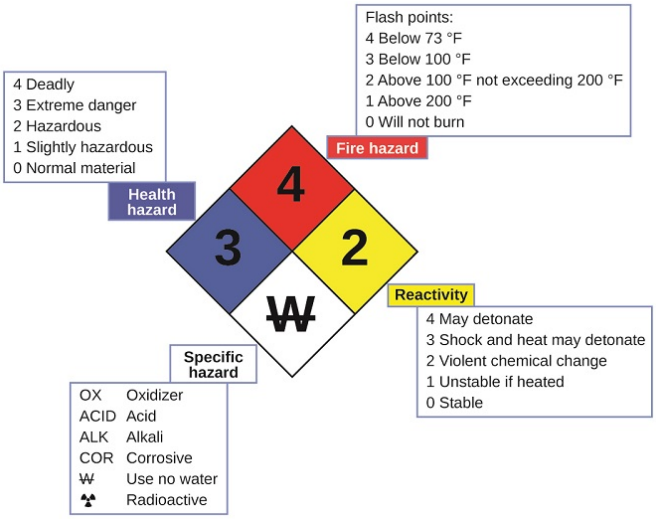


Figure **9.2.3.4**: The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. We can identify sets of elements that exhibit common behaviors. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have properties of both metals and nonmetals).

The periodic table is a table of elements that places elements with similar properties close together (Figure **9.2.3.5**). You will learn more about the periodic table as you continue your study of chemistry.

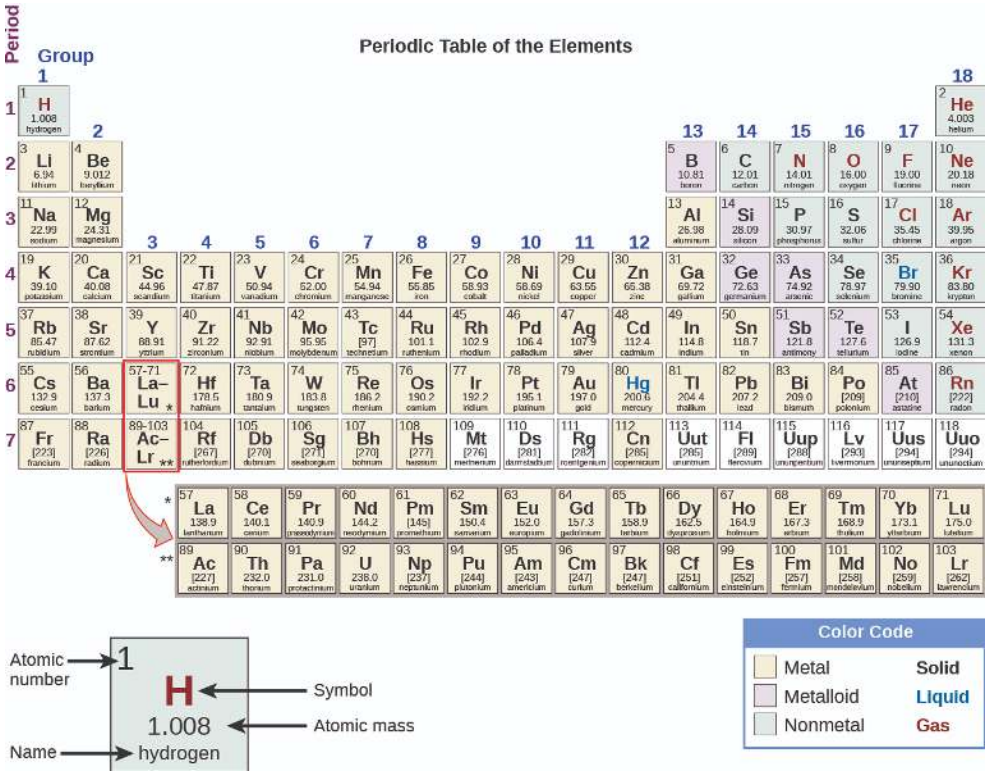


Figure 9.2.3.5: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Contributors and Attributions

Summary

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

Glossary

chemical change

change producing a different kind of matter from the original kind of matter

chemical property

behavior that is related to the change of one kind of matter into another kind of matter

extensive property

property of a substance that depends on the amount of the substance

intensive property

property of a substance that is independent of the amount of the substance

physical change

change in the state or properties of matter that does not involve a change in its chemical composition

physical property

characteristic of matter that is not associated with any change in its chemical composition

Contributors and Attributions

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9.2.4: Measurements

Learning Objectives

- Explain the process of measurement
- Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5×10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 9.2.4.1. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the International System of Units or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Table 9.2.4.1: Base Units of the SI System

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

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 9.2.4.2.

Table 9.2.4.2: Common Unit Prefixes

Prefix	Symbol	Factor	Example
femto	f	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)
pico	p	10^{-12}	1 picometer (pm) = 1×10^{-12} m (0.000000000001 m)
nano	n	10^{-9}	4 nanograms (ng) = 4×10^{-9} g (0.000000004 g)
micro	μ	10^{-6}	1 microliter (μL) = 1×10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2×10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7×10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1×10^{-1} L (0.1 L)
kilo	k	10^{3}	1 kilometer (km) = 1×10^{3} m (1000 m)
mega	M	10^{6}	3 megahertz (MHz) = 3×10^{6} Hz (3,000,000 Hz)
giga	G	10^{9}	8 gigayears (Gyr) = 8×10^{9} yr (8,000,000,000 Gyr)
tera	T	10^{12}	5 terawatts (TW) = 5×10^{12} W (5,000,000,000,000 W)

SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

Length

The standard unit of length in both the SI and original metric systems is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure **9.2.4.1**); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers (1 km = 1000 m = 10^3 m), whereas shorter distances can be reported in centimeters (1 cm = 0.01 m = 10^{-2} m) or millimeters (1 mm = 0.001 m = 10^{-3} m).

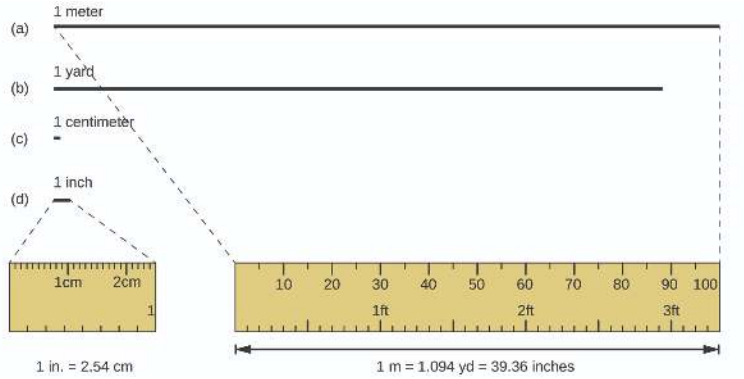


Figure **9.2.4.1**: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

The standard unit of mass in the SI system is the kilogram (kg). A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France (Figure 1.4.2). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).



Figure **9.2.4.2**: This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology).

Temperature

Temperature is an intensive property. The SI unit of temperature is the kelvin (K). The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°). The degree Celsius (°C) is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

Time

The SI base unit of time is the second (s). Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^{6} s. Alternatively, hours, days, and years can be used.

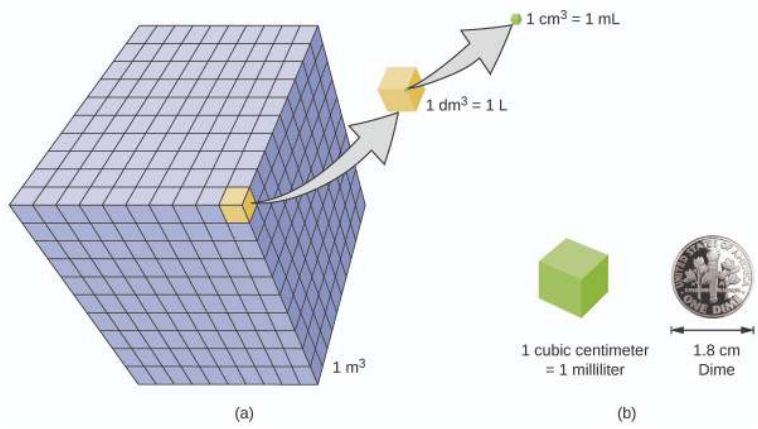
Derived SI Units

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure **9.2.4.3**). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. One liter is about 1.06 quarts. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.



<

Figure **9.2.4.3**: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table **9.2.4.3** shows the densities of some common substances.

Table **9.2.4.3**: Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{9.2.4.1}$$

Example 9.2.4.1

Calculation of Density Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

$$\text{volume of lead cube} = 2.00\ \text{cm} \times 2.00\ \text{cm} \times 2.00\ \text{cm} = 8.00\ \text{cm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7\ \text{g}}{8.00\ \text{cm}^3} = \frac{11.3\ \text{g}}{1.00\ \text{cm}^3} = 11.3\ \text{g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

Exercise 9.2.4.1

a. To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm?
b. If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

Answer a

0.599 cm^3;

Answer b

8.91 g/cm^3

Example 9.2.4.2: Using Displacement of Water to Determine Density

This PhET simulation illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{1.25\ \text{L}} = 4.00\ \text{kg/L} \tag{9.2.4.2}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{10.00\ \text{L}} = 0.500\ \text{kg/L} \tag{9.2.4.3}$$

Exercise 9.2.4.1

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Answer

2.00 kg/L

Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^6 hertz), respectively.

Key Equations

- $\text{density} = \frac{\text{mass}}{\text{volume}}$

Glossary

Celsius (°C)
unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm^3 or cc)
volume of a cube with an edge length of exactly 1 cm

cubic meter (m^3)
SI unit of volume

density
ratio of mass to volume for a substance or object

kelvin (K)
SI unit of temperature; 273.15 K = 0 ºC

kilogram (kg)
standard SI unit of mass; 1 kg = approximately 2.2 pounds

length
measure of one dimension of an object

liter (L)
(also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

meter (m)
standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)
1/1,000 of a liter; equal to 1 cm^3

second (s)

SI unit of time

SI units (International System of Units)

standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit

standard of comparison for measurements

volume

amount of space occupied by an object

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9.2.5: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

- Define accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an exact number. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

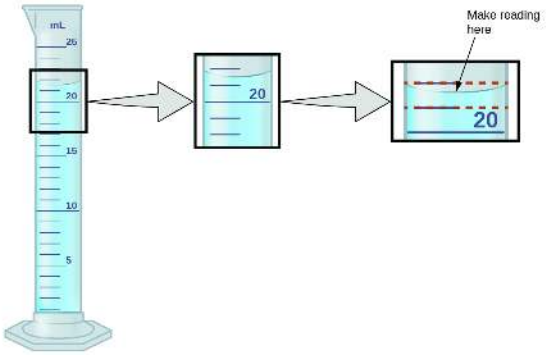
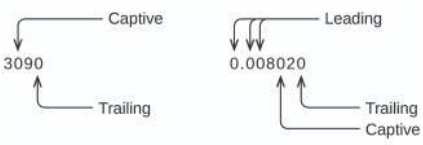


Figure 9.2.5.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

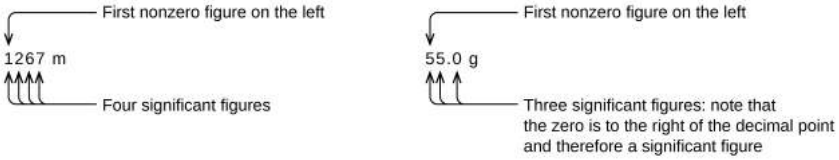
Refer to the illustration in Figure **9.2.5.1**. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some uncertainty, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called significant figures or significant digits. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms “leading,” “trailing,” and “captive” for the zeros and will consider how to deal with them.



Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.

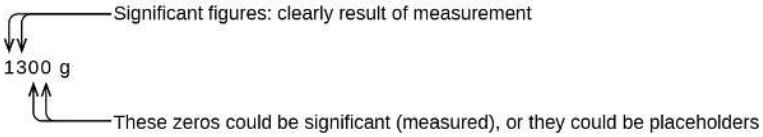


Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.



When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely—that is, whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 317 million, or $\mathbf{3.17 \times 10^8}$ people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for rounding numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we "round down" and leave the retained digit unchanged; if it is more than 5, we "round up" and increase the retained digit by 1; if the dropped digit *is* 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it's based on reliable statistics and is aimed at avoiding any bias when dropping the digit "5," since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds "up" to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds "down" to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds "up" to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds "down" to 92.8 (the dropped digit is 5, and the retained digit is even)

Let's work through these rules with a few examples.

Example 9.2.5.1: Rounding Numbers

Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)
b. 8.1649 (to three significant figures)
c. 0.051065 (to four significant figures)
d. 0.90275 (to four significant figures)

Solution

a. 31.57 rounds "up" to 32 (the dropped digit is 5, and the retained digit is even)
b. 8.1649 rounds "down" to 8.16 (the dropped digit, 4, is less than 5)
c. 0.051065 rounds "down" to 0.05106 (the dropped digit is 5, and the retained digit is even)
d. 0.90275 rounds "up" to 0.9028 (the dropped digit is 5, and the retained digit is even)

Exercise 9.2.5.1

Round the following to the indicated number of significant figures:

a. 0.424 (to two significant figures)
b. 0.0038661 (to three significant figures)
c. 421.25 (to four significant figures)
d. 28,683.5 (to five significant figures)

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

Example 9.2.5.2: Addition and Subtraction with Significant Figures Rule:

When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).

a. Add 1.0023 g and 4.383 g.
b. Subtract 421.23 g from 486 g.

Solution

(a)

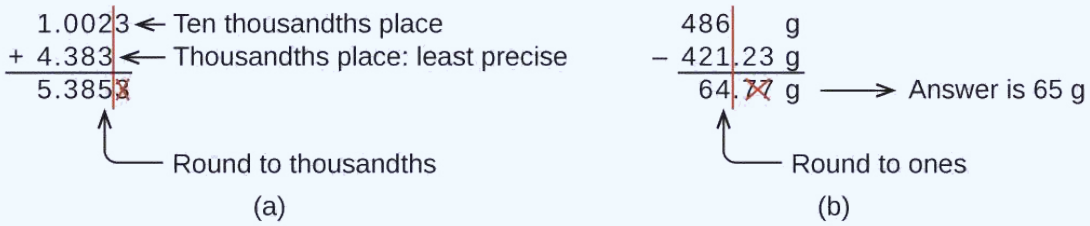
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{r} 486\ \text{g} \\ -\ 421.23\ \text{g} \\ \hline 64.77\ \text{g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)



Exercise 9.2.5.2

a. Add 2.334 mL and 0.31 mL.
b. Subtract 55.8752 m from 56.533 m.

Answer a

2.64 mL

Answer b

0.658 m

Example 9.2.5.3: Multiplication and Division with Significant Figures

Rule: When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

a. Multiply 0.6238 cm by 6.6 cm.
b. Divide 421.23 g by 486 mL.

Solution

(a)

$$0.6238\ \text{cm} \times 6.6\ \text{cm} = 4.11708\ \text{cm}^2 \rightarrow \text{result is } 4.1\ \text{cm}^2 \quad (9.2.5.1)$$
$$\text{(round to two significant figures)}$$

$$\text{four significant figures} \times \text{two significant figures} \rightarrow \text{two significant figures answer} \tag{9.2.5.2}$$

(b)

$$\frac{421.23\ \text{g}}{486\ \text{mL}} = 0.86728...\ \text{g/mL} \rightarrow \text{result is } 0.867\ \text{g/mL} \quad \text{(round to three significant figures)} \tag{9.2.5.3}$$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer} \tag{9.2.5.4}$$

Exercise 9.2.5.3

a. Multiply 2.334 cm and 0.320 cm.
b. Divide 55.8752 m by 56.53 s.

Answer a

0.747 cm^2

Answer b

0.9884 m/s

In the midst of all these technicalities, it is important to keep in mind the reason why we use significant figures and rounding rules—to correctly represent the certainty of the values we report and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example 9.2.5.4: Calculation with Significant Figures

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44\ \text{dm} \times 5.920\ \text{dm} \times 2.54\ \text{dm} \\ &= 202.09459...\text{dm}^3\ \text{(value from calculator)} \\ &= 202\ \text{dm}^3\text{, or } 202\ \text{L (answer rounded to three significant figures)} \end{aligned}$$

Exercise 9.2.5.4: Determination of Density Using Water Displacement

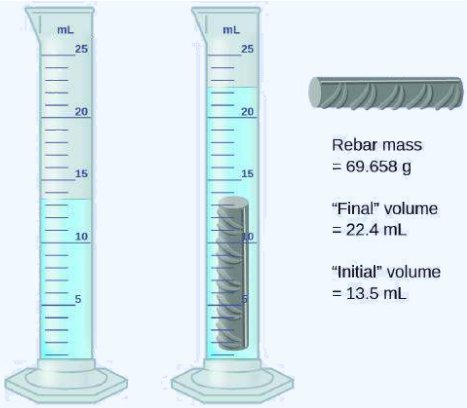
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 9.2.5.4

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



a. Use these values to determine the density of this piece of rebar.
b. Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

$$\text{volume} = 22.4\ \text{mL} - 13.5\ \text{mL} = 8.9\ \text{mL} = 8.9\ \text{cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658\ \text{g}}{8.9\ \text{cm}^3} = 7.8\ \text{g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)

The density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Exercise 9.2.5.4

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.



a. Use these values to determine the density of this material.
b. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Answer a

19 g/cm^3

Answer b

It is likely gold; it has the right appearance for gold and very close to the density given for gold.

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure **9.2.5.2**).

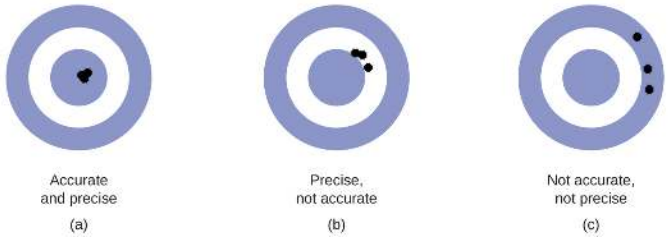


Figure **9.2.5.2**: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table **9.2.5.2**.

Table **9.2.5.2**: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Glossary

uncertainty

estimate of amount by which measurement differs from true value

significant figures

(also, significant digits) all of the measured digits in a determination, including the uncertain last digit

rounding

procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

precision

how closely a measurement matches the same measurement when repeated

exact number

number derived by counting or by definition

accuracy

how closely a measurement aligns with a correct value

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9.2.6: Mathematical Treatment of Measurement Results

Learning Objectives

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities
- Use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

$$\text{speed} = \frac{\text{distance}}{\text{time}} \tag{9.2.6.1}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

$$\frac{100\ \text{m}}{10\ \text{s}} = 10\ \text{m/s} \tag{9.2.6.2}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

$$\text{time} = \frac{\text{distance}}{\text{speed}} \tag{9.2.6.3}$$

The time can then be computed as:

$$\frac{25\ \text{m}}{10\ \text{m/s}} = 2.5\ \text{s} \tag{9.2.6.4}$$

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as dimensional analysis (or the factor-label method). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a unit conversion factor. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

$$\frac{2.54\ \text{cm}}{1\ \text{in.}}\ (2.54\ \text{cm} = 1\ \text{in.})\ \text{or}\ 2.54\ \frac{\text{cm}}{\text{in.}} \tag{9.2.6.5}$$

Several other commonly used conversion factors are given in Table 9.2.6.1.

Table 9.2.6.1: Common Conversion Factors

Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

When we multiply a quantity (such as distance given in inches) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

$$34 \cancel{\text{in.}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{in.}}} = 86 \text{ cm} \tag{9.2.6.6}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield

$$\frac{\text{in.} \times \text{cm}}{\text{in.}}. \tag{9.2.6.7}$$

Just as for numbers, a ratio of identical units is also numerically equal to one,

$$\frac{\text{in.}}{\text{in.}} = 1 \tag{9.2.6.8}$$

and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to "cancel.") Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

Example 9.2.6.1: Using a Unit Conversion Factor

The mass of a competition Frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 9.2.6.1).

Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimeters.

$$x \text{ oz} = 125 \text{ g} \times \text{unit conversion factor}$$

We write the unit conversion factor in its two forms:

$$\frac{1 \text{ oz}}{28.349 \text{ g}} \text{ and } \frac{28.349 \text{ g}}{1 \text{ oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

$$\begin{aligned} x \text{ oz} &= 125 \cancel{\text{g}} \times \frac{1 \text{ oz}}{28.349 \cancel{\text{g}}} \\ &= \left(\frac{125}{28.349}\right) \text{ oz} \\ &= 4.41 \text{ oz (three significant figures)} \end{aligned}$$

Exercise 9.2.6.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 9.2.6.2: Computing Quantities from Measurement Results

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

Solution

Since $\text{density} = \dfrac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A × unit conversion factor. The necessary conversion factors are given in Table 1.7.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:

$$9.26 \cancel{\text{lb}} \times \frac{453.59\ \text{g}}{1\ \cancel{\text{lb}}} = 4.20 \times 10^3\ \text{g}$$

We need to use two steps to convert volume from quarts to milliliters.

1. *Convert quarts to liters.*

$$4.00\ \cancel{\text{qt}} \times \frac{1\ \text{L}}{1.0567\ \cancel{\text{qt}}} = 3.78\ \text{L}$$

2. *Convert liters to milliliters.*

$$3.78\ \cancel{\text{L}} \times \frac{1000\ \text{mL}}{1\ \cancel{\text{L}}} = 3.78 \times 10^3\ \text{mL}$$

Then,

$$\text{density} = \frac{4.20 \times 10^3\ \text{g}}{3.78 \times 10^3\ \text{mL}} = 1.11\ \text{g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

$$\frac{9.26\ \cancel{\text{lb}}}{4.00\ \cancel{\text{qt}}} \times \frac{453.59\ \text{g}}{1\ \cancel{\text{lb}}} \times \frac{1.0567\ \cancel{\text{qt}}}{1\ \cancel{\text{L}}} \times \frac{1\ \cancel{\text{L}}}{1000\ \text{mL}} = 1.11\ \text{g/mL}$$

Exercise 9.2.6.2

What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Answer

$2.956 \times 10^{-2}\ \text{L}$

Example 9.2.6.3: Computing Quantities from Measurement Results

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

a. What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?
b. If gasoline costs $3.80 per gallon, what was the fuel cost for this trip?

Solution

(a) We first convert distance from kilometers to miles:

$$1250\ \text{km} \times \frac{0.62137\ \text{mi}}{1\ \text{km}} = 777\ \text{mi}$$

and then convert volume from liters to gallons:

$$213\ \cancel{\text{L}} \times \frac{1.0567\ \cancel{\text{qt}}}{1\ \cancel{\text{L}}} \times \frac{1\ \text{gal}}{4\ \cancel{\text{qt}}} = 56.3\ \text{gal}$$

Then,

$$\text{(average) mileage} = \frac{777\ \text{mi}}{56.3\ \text{gal}} = 13.8\ \text{miles/gallon} = 13.8\ \text{mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

$$\frac{1250\ \cancel{\text{km}}}{213\ \cancel{\text{L}}} \times \frac{0.62137\ \text{mi}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{L}}}{1.0567\ \cancel{\text{qt}}} \times \frac{4\ \cancel{\text{qt}}}{1\ \text{gal}} = 13.8\ \text{mpg}$$

(b) Using the previously calculated volume in gallons, we find:

$$56.3\ \text{gal} \times \frac{\$3.80}{1\ \text{gal}} = \$214$$

Exercise 9.2.6.3

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

a. What (average) fuel economy, in miles per gallon, did the Prius get during this trip?
b. If gasoline costs $3.90 per gallon, what was the fuel cost for this trip?

Answer a

51 mpg

Answer b

$62

Conversion of Temperature Units

We use the word temperature to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes. Because the volume of the liquid changes more than the volume of the glass, we can see the liquid expand when it gets warmer and contract when it gets cooler.

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which

we call degrees. On the Fahrenheit scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

$$\text{length in feet} = \left(\frac{1\ \text{ft}}{12\ \text{in.}}\right) \times \text{length in inches} \tag{9.2.6.9}$$

where

- y = length in feet,
- x = length in inches, and
- the proportionality constant, m, is the conversion factor.

The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one ($y = mx + b$). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as x and the Fahrenheit temperature as y, the slope, m, is computed to be:

$$\begin{aligned} m &= \frac{\Delta y}{\Delta x} \\ &= \frac{212\ ^\circ\text{F} - 32\ ^\circ\text{F}}{100\ ^\circ\text{C} - 0\ ^\circ\text{C}} \\ &= \frac{180\ ^\circ\text{F}}{100\ ^\circ\text{C}} \\ &= \frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \end{aligned}$$

The y-intercept of the equation, b, is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

$$\begin{aligned} b &= y - mx \\ &= 32\ ^\circ\text{F} - \frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \times 0\ ^\circ\text{C} \\ &= 32\ ^\circ\text{F} \end{aligned}$$

The equation relating the temperature scales is then:

$$T_{^\circ\text{F}} = \left(\frac{9\ ^\circ\text{F}}{5\ ^\circ\text{C}} \times T_{^\circ\text{C}}\right) + 32\ ^\circ\text{C} \tag{9.2.6.10}$$

An abbreviated form of this equation that omits the measurement units is:

$$T_{^\circ\text{F}} = \frac{9}{5} \times T_{^\circ\text{C}} + 32 \tag{9.2.6.11}$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

$$T_{^\circ\text{C}} = \frac{5}{9}(T_{^\circ\text{F}} + 32) \tag{9.2.6.12}$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at −273.15 °C. In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin,

proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of $1\ \frac{\text{K}}{^\circ\text{C}}$. Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

$$T_{\text{K}} = T_{^\circ\text{C}} + 273.15 \tag{9.2.6.13}$$

$$T_{^\circ\text{C}} = T_{\text{K}} - 273.15 \tag{9.2.6.14}$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure **9.2.6.1** shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

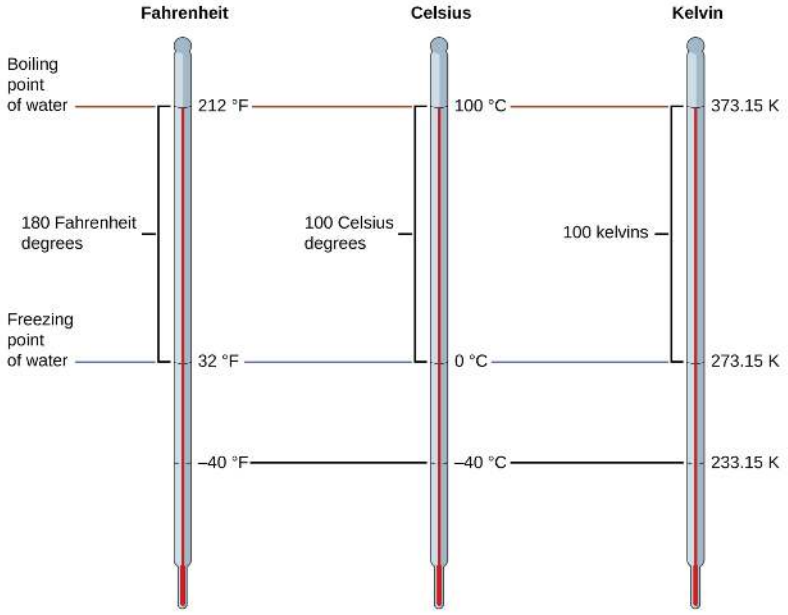


Figure 9.2.6.1: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

Example 9.2.6.4: Conversion from Celsius

Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on the Fahrenheit scale?

Solution

$$\text{K} = ^\circ\text{C} + 273.15 = 37.0 + 273.2 = 310.2\ \text{K}$$

$$^\circ\text{F} = \frac{9}{5}\ ^\circ\text{C} + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6\ ^\circ\text{F}$$

Exercise 9.2.6.4

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

Example 9.2.6.5: Conversion from Fahrenheit

Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?

Solution

$$°\text{C} = \frac{5}{9}(°\text{F} - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232°\text{C} \rightarrow \text{set oven to } 230°\text{C}$$
$$\text{(two significant figures)}$$

$$\text{K} = °\text{C} + 273.15 = 230 + 273 = 503\ \text{K} \rightarrow 5.0 \times 10^2\ \text{K} \quad \text{(two significant figures)}$$

Exercise 9.2.6.5

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

Summary

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

Key Equations

- $T_{°\text{C}} = \frac{5}{9} \times T_{°\text{F}} - 32$
- $T_{°\text{F}} = \frac{9}{5} \times T_{°\text{C}} + 32$
- $T_{\text{K}} = °\text{C} + 273.15$
- $T_{°\text{C}} = \text{K} - 273.15$

Glossary

dimensional analysis

(also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit

unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

unit conversion factor

ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

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SECTION OVERVIEW

0.3: Atoms, Molecules, and Ions

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General Chemistry

This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

9.3.1: Atomic Structure and Symbolism

9.3.2: Chemical Formulas

9.3.3: The Periodic Table

9.3.4: Molecular and Ionic Compounds

9.3.5: Chemical Nomenclature

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Thumbnail: Spinning Buckminsterfullerene (C_{60}). (CC BY-SA 3.0; unported; Sponk).

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9.3.1: Atomic Structure and Symbolism

Learning Objectives

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure **9.3.1.1**).



Figure **9.3.1.1**: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly **1/12** of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table **9.3.1.1**. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table **9.3.1.1**: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

The number of protons in the nucleus of an atom is its atomic number (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\begin{aligned} \text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ \text{A} - \text{Z} &= \text{number of neutrons} \end{aligned}$$

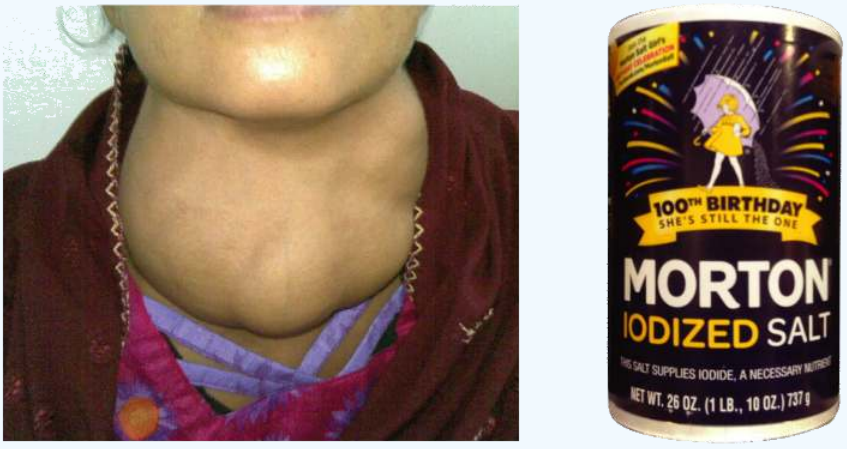
Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge (8 − 10 = 2−).

Example 9.3.1.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 9.3.1.2).



(a) (b)

Figure 9.3.1.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 − 53 = 74). Since the iodine is added as a 1− anion, the number of electrons is 54 [53 – (1–) = 54].

Exercise 9.3.1.1

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure **9.3.1.3**). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure **9.3.1.3**: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table **9.3.1.2**. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table **9.3.1.2**: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists or locations; for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure **9.3.1.4**). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

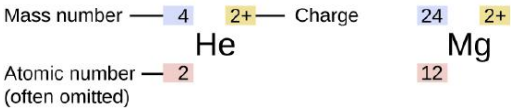


Figure **9.3.1.4**: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table **9.3.1.2**. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table **9.3.1.2**: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}\mathrm{H}$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.25

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i \tag{9.3.1.1}$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129\ \text{amu}) + (0.801 \times 11.0093\ \text{amu}) \\ &= 1.99\ \text{amu} + 8.82\ \text{amu} \\ &= 10.81\ \text{amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example 9.3.1.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924\ \text{amu}) + (0.0047 \times 20.9940\ \text{amu}) + (0.0769 \times 21.9914\ \text{amu}) \\ &= (18.36 + 0.099 + 1.69)\ \text{amu} \\ &= 20.15\ \text{amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Exercise 9.3.1.2

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Answer

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

Example 9.3.1.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\begin{aligned}&\text{average mass} \\ &= (\text{fraction of } {}^{35}\text{Cl} \times \text{mass of } {}^{35}\text{Cl}) + (\text{fraction of } {}^{37}\text{Cl} \times \text{mass of } {}^{37}\text{Cl})\end{aligned} \tag{9.3.1.2}$$

If we let x represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by $1.00 - x$.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 − the fraction of ^{35}Cl.)

Substituting this into the average mass equation, we have:

$$\begin{aligned}35.453\ \text{amu} &= (x \times 34.96885\ \text{amu}) + [(1.00 - x) \times 36.96590\ \text{amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576\end{aligned}$$

So solving yields: $x = 0.7576$, which means that $1.00 - 0.7576 = 0.2424$. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

Exercise 9.3.1.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer

69.15% Cu-63 and 30.85% Cu-65

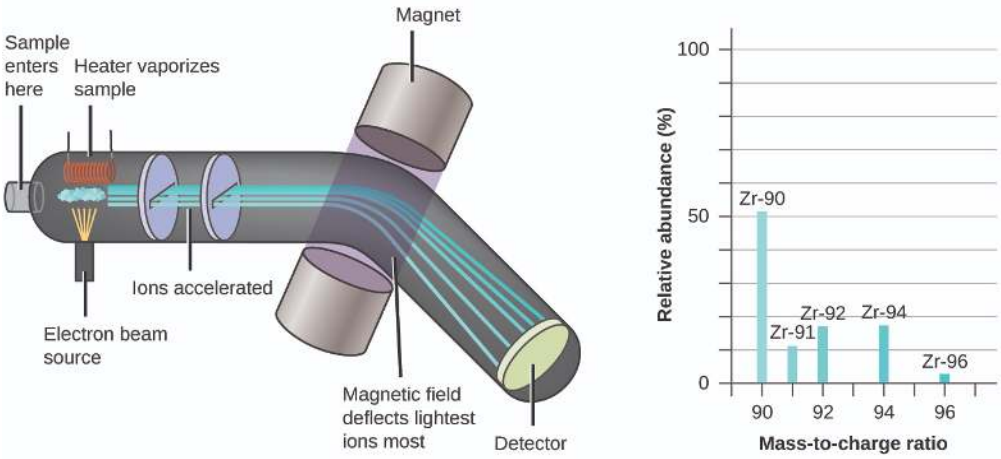


Figure 9.3.1.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 9.3.1.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



***Video* 9.3.1.1**: *Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $\mathbf{1/12}$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

- $\textbf{average mass} = \sum_i (\textbf{fractional abundance} \times \textbf{isotopic mass})_i$

Glossary

anion
negatively charged atom or molecule (contains more electrons than protons)

atomic mass
average mass of atoms of an element, expressed in amu

atomic mass unit (amu)
(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)
number of protons in the nucleus of an atom

cation
positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol
one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)
alternative unit equivalent to the atomic mass unit

fundamental unit of charge
(also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C

ion
electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)
sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

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9.3.2: Chemical Formulas

Learning Objectives

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

A molecular formula is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure **9.3.2.1**). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

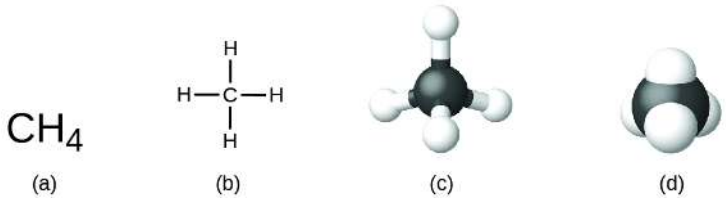


Figure **9.3.2.1**: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure **9.3.2.2**).

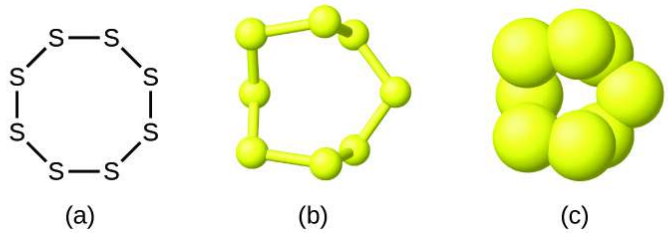


Figure **9.3.2.2**: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure **9.3.2.3**).

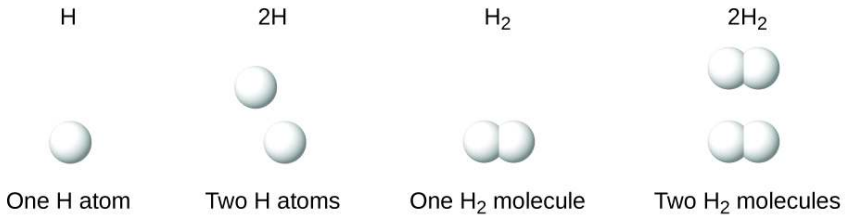


Figure **9.3.2.3**: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure **9.3.2.4**).

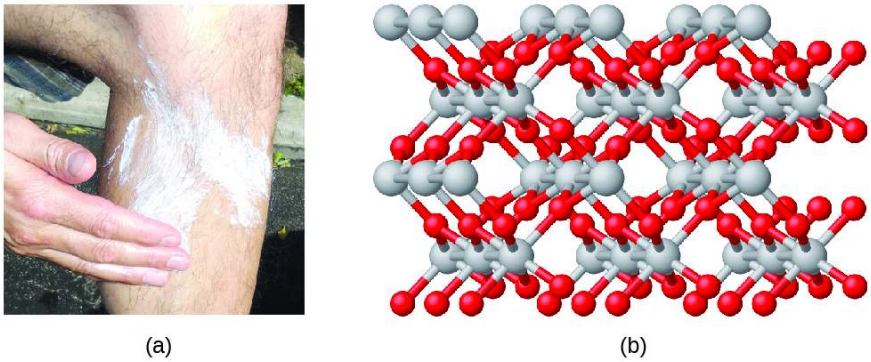


Figure **9.3.2.4**: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr).

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure **9.3.2.5**).

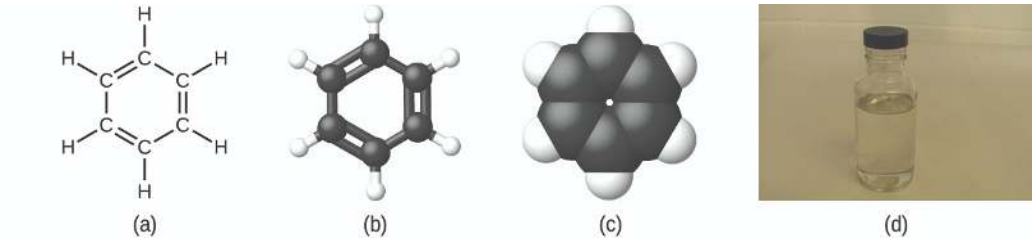


Figure **9.3.2.5**: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

If we know a compound’s formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure **9.3.2.6**) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common

denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.

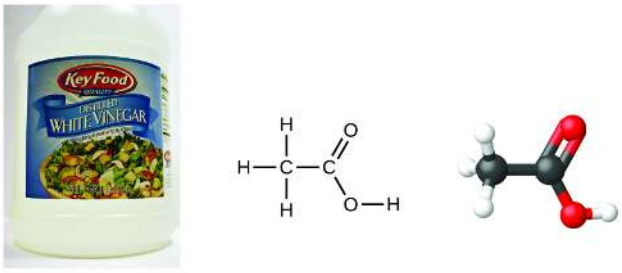


Figure **9.3.2.6**: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Example 9.3.2.1: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

Exercise 9.3.2.1

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of isomers—compounds with the same chemical formula but different molecular structures (Figure **9.3.2.7**). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.

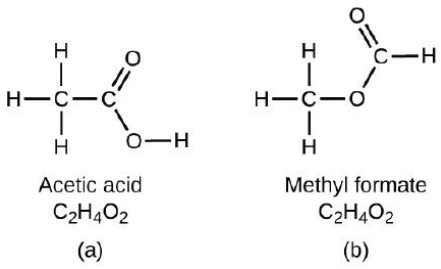


Figure **9.3.2.7**: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 9.3.2.8). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.

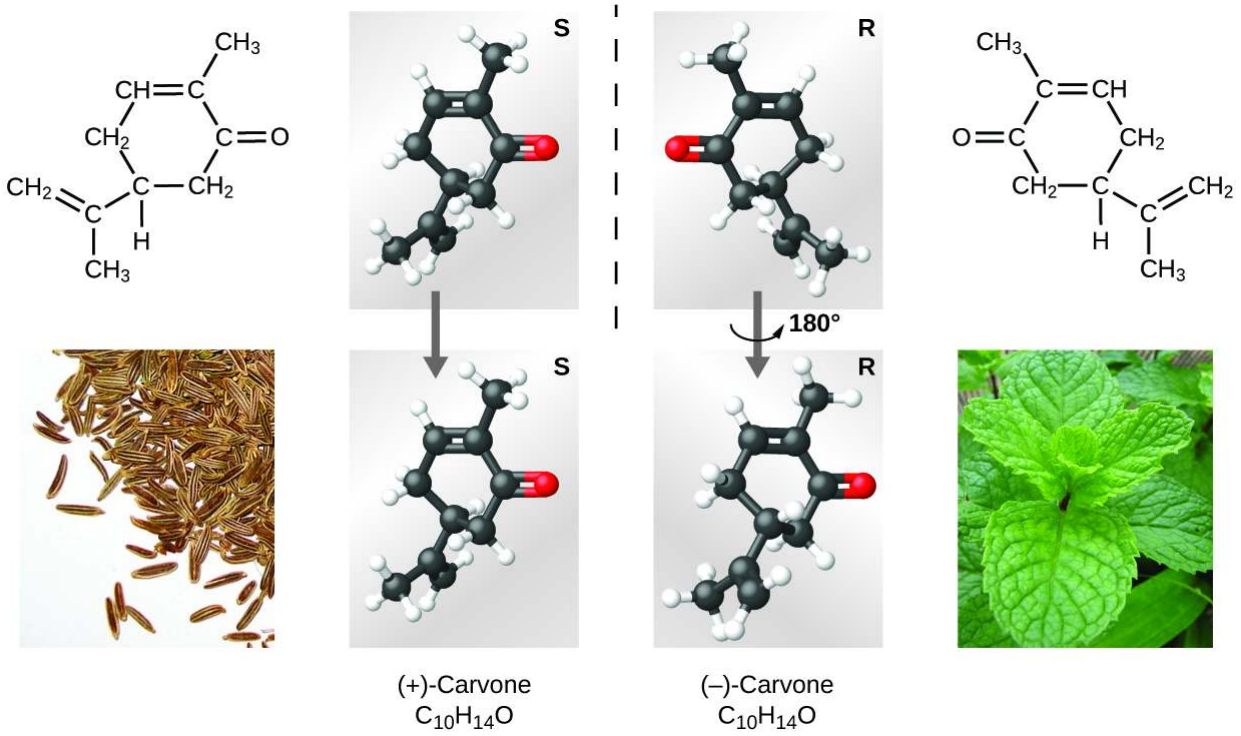


Figure 9.3.2.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

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Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Glossary

empirical formula
formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers
compounds with the same chemical formula but different structures

molecular formula
formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers
compounds in which the relative orientations of the atoms in space differ

structural isomer

one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

structural formula

shows the atoms in a molecule and how they are connected

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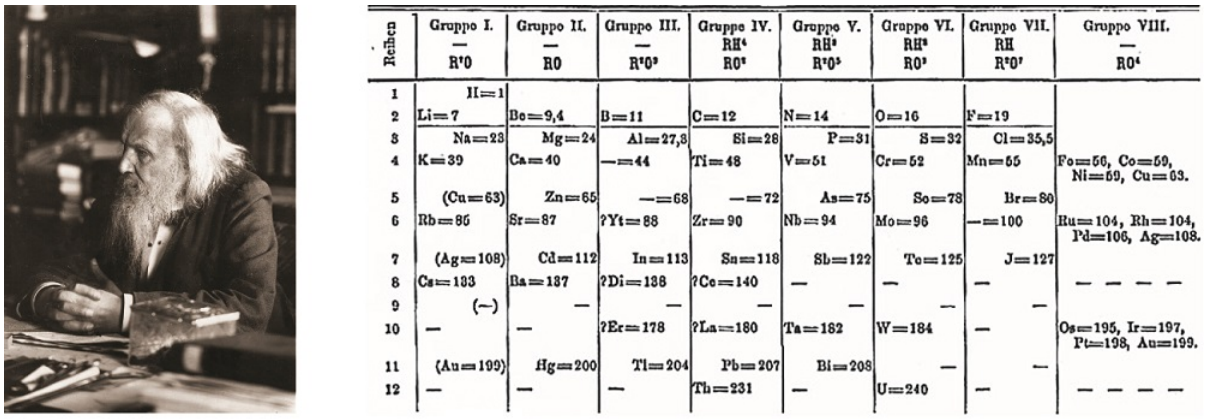
9.3.3: The Periodic Table

Learning Objectives

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure **9.3.3.1**).



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	—	— — — —

(a) (b)

Figure **9.3.3.1**: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure **9.3.3.2**). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

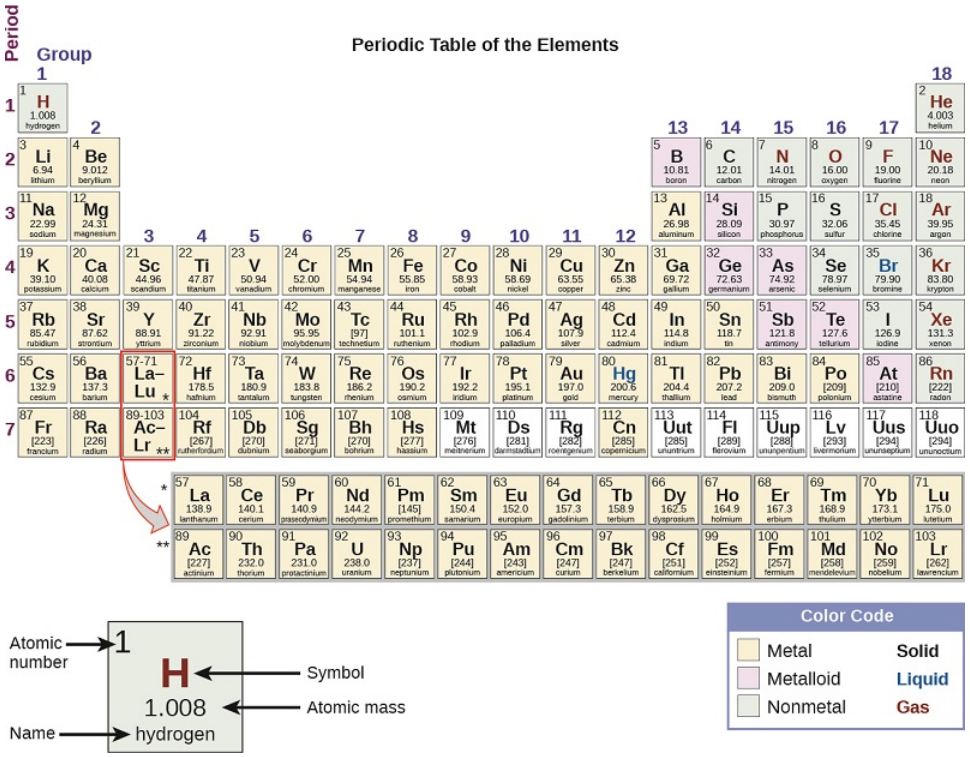


Figure **9.3.3.2**: Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: metals (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure **9.3.3.3**). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

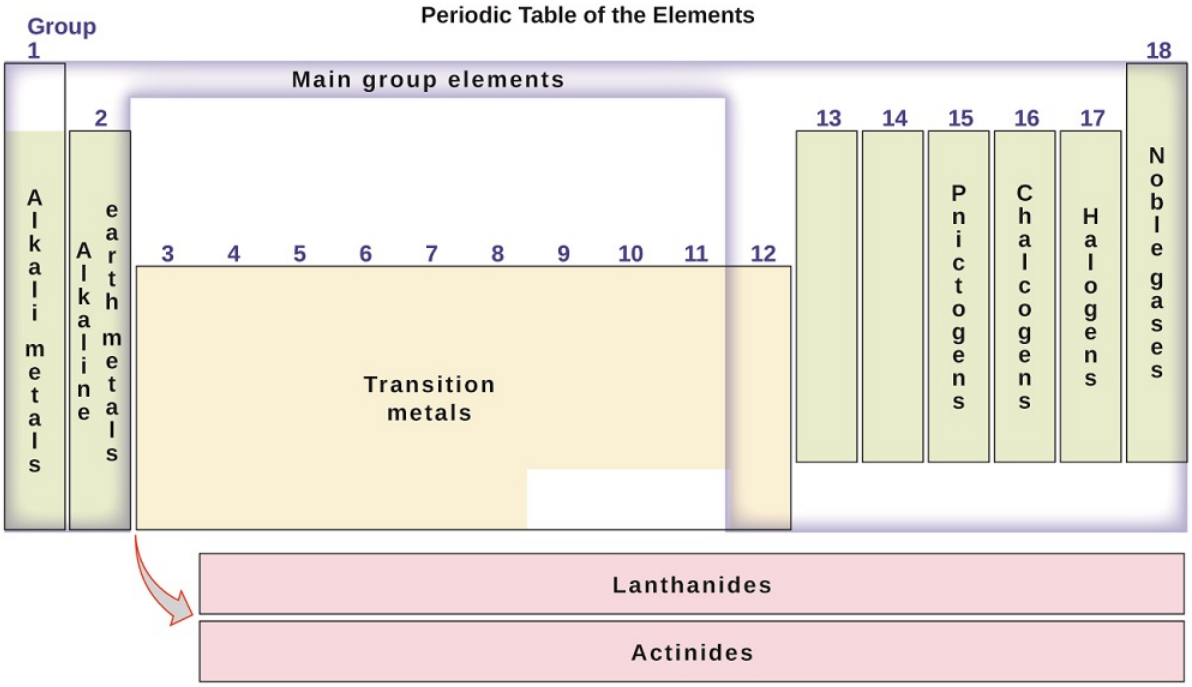


Figure 9.3.3.3: The periodic table organizes elements with similar properties into groups.

Example 9.3.3.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

Exercise 9.3.3.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

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Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Glossary

actinide
inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element

(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law
properties of the elements are periodic function of their atomic numbers.

periodic table
table of the elements that places elements with similar chemical properties close together

pnictogen
element in group 15

representative element
(also, main-group element) element in columns 1, 2, and 12–18

transition metal
element in columns 3–11

series
(also, period) horizontal row of the period table

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9.3.4: Molecular and Ionic Compounds

Learning Objectives

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure **9.3.4.1**).

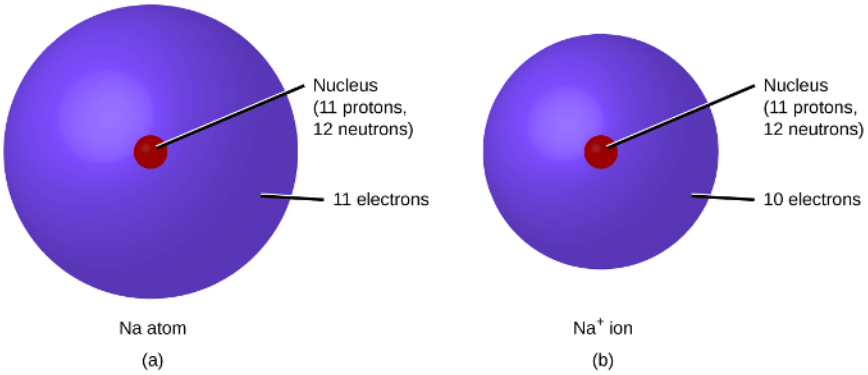


Figure **9.3.4.1**: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure **9.3.4.2**). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

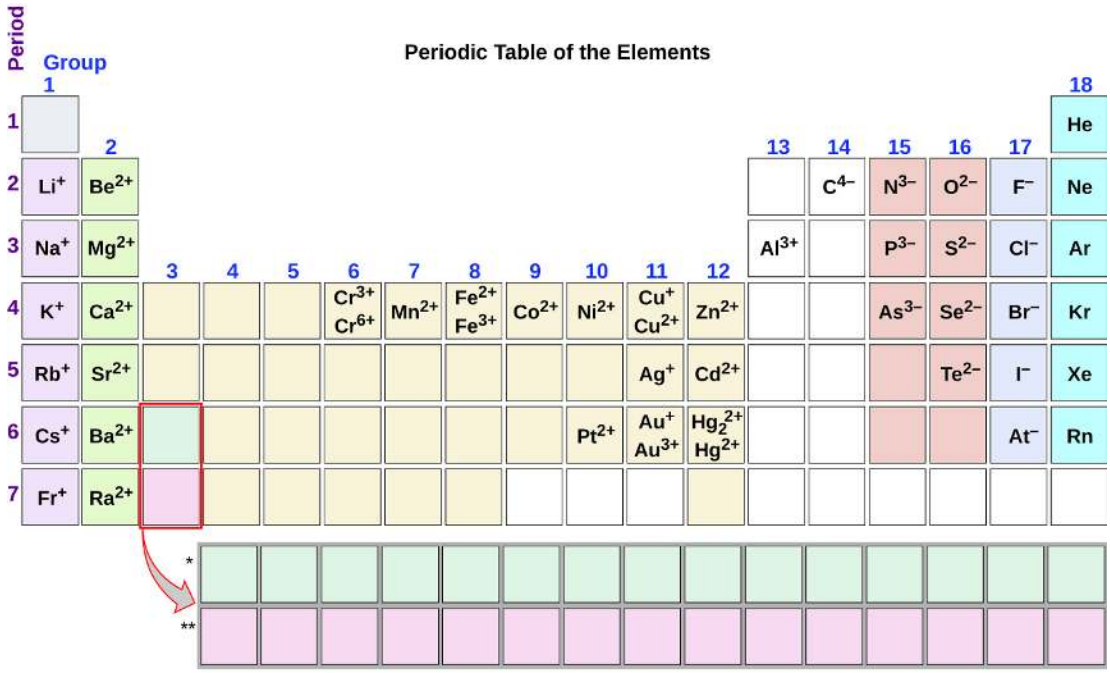


Figure **9.3.4.2**: Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 9.3.4.1: Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Exercise 9.3.4.1

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer

Se^{2-}, the selenide ion

Example 9.3.4.2: Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

Exercise **9.3.4.2**

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table **9.3.4.1**. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table **9.3.4.1**: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for “hyper”) and *hypo-* (meaning “under”) are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^- and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are “shared” and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei

of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an ionic compound. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure **9.3.4.3**).

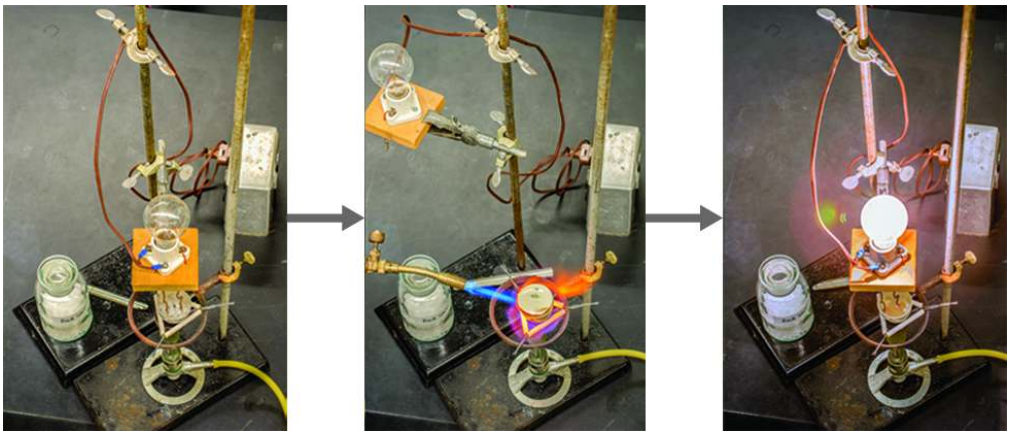


Figure **9.3.4.3**: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example **9.3.4.3**: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure **9.3.4.4**) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure **9.3.4.4**: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

Exercise 9.3.4.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table **9.3.4.1**) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate ($\mathbf{PO_4^{3-}}$) groups. The $\mathbf{PO_4^{3-}}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 9.3.4.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $\mathbf{H_2PO_4^-}$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $\mathbf{H_2PO_4^-}$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 9.3.4.4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, $\mathbf{O_2^{2-}}$ (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and

$C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These molecular compounds (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example 9.3.4.5: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

a. KI, the compound used as a source of iodine in table salt
b. H_2O_2, the bleach and disinfectant hydrogen peroxide
c. $CHCl_3$, the anesthetic chloroform
d. Li_2CO_3, a source of lithium in antidepressants

Solution

a. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Exercise 9.3.4.5

Using the periodic table, predict whether the following compounds are ionic or covalent:

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

Glossary

covalent bond
attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound
(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion
ion composed of a single atom

polyatomic ion
ion composed of more than one atom

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

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9.3.5: Chemical Nomenclature

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly. We will begin with the nomenclature rules for ionic compounds.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table **9.3.5.2**.

Table **9.3.5.1**: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table **9.3.5.2**.

Table **9.3.5.2**: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table **9.3.5.3**. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 9.3.5.3: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt
KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+, and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 9.3.5.4.

Table 9.3.5.4: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more

properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 9.3.5.1: Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^-, and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 9.3.5.1

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. chromium(VI) fluoride

Answer a

CrP

Answer b

HgS

Answer c

$Mn_3(PO_4)_2$

Answer d

Cu_2O

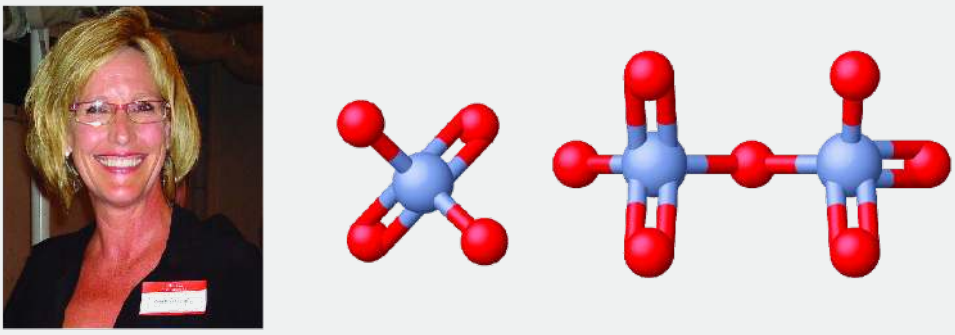
Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 9.3.5.2) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in

1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a) (b)

Figure 9.3.5.2: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $Cr_2O_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. Cr(VI), on the other hand, is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table **9.3.5.5**.

Table **9.3.5.5**: Nomenclature Prefixes

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table **9.3.5.6**.

Table **9.3.5.6**: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphoru

Compound	Name	Compound	Name
			sentafluoride
N_2O_4	dinitrogen tetroxide	P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide	IF_7	iodin

Compound	Name	Compound	Name
			heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

Example 9.3.5.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

Exercise 9.3.5.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer a

PCl_5

Answer b

N_2O

Answer c

IF_7

Answer d

CCl_4

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas **HCl** (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table **9.3.5.7**.

Table **9.3.5.7**: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(*g*), hydrogen fluoride	HF(*aq*), hydrofluoric acid
HCl(*g*), hydrogen chloride	HCl(*aq*), hydrochloric acid
HBr(*g*), hydrogen bromide	HBr(*aq*), hydrobromic acid
HI(*g*), hydrogen iodide	HI(*aq*), hydroiodic acid
H_2S(*g*), hydrogen sulfide	H_2S(*aq*), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as oxyacids, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table **9.3.5.8**. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table **9.3.5.8**: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

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Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *–ic*, and *-ite* to *-ous*) and adding "acid;" H_2CO_3 is carbonic acid.

Glossary

binary acid
: compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound
: compound containing two different elements.

oxyacid
: compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

nomenclature
: system of rules for naming objects of interest

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CHAPTER OVERVIEW

1.1: Stoichiometry- Chemical Formulas and Equations

Stoichiometry is the calculation of relative quantities of reactants and products in chemical reactions. Stoichiometry is founded on the **law of conservation of mass** where the total mass of the reactants equals the total mass of the products leading to the insight that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Conversely, if one reactant has a known quantity and the quantity of product can be empirically determined, then the amount of the other reactants can also be calculated.

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.

1.1.1: Chemical Equations
1.1.2: Some Simple Patterns of Chemical Reactivity
1.1.3: Avogadro's Number and the Mole
1.1.4: Empirical and Molecular Formulas
1.1.5: Empirical Formulas from Analysis
1.1.6: Reaction Stoichiometry
1.1.7: Limiting Reactants

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1.1.1: Chemical Equations

Learning Objectives

- To describe a chemical reaction.
- To calculate the quantities of compounds produced or consumed in a chemical reaction

What happens to matter when it undergoes chemical changes? The Law of conservation of mass says that "***Atoms are neither created, nor distroyed, during any chemical reaction***." Thus, the same collection of atoms is present after a reaction as before the reaction. The changes that occur during a reaction just involve the *rearrangement* of atoms. In this section we will discuss ***stoichiometry*** (the "measurement of elements").

Chemical Equations

As shown in Figure **1.1.1.1**, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. This reaction is described with a chemical equation, an expression that gives the identities and quantities of the substances in a chemical reaction.



Figure* 1.1.1.1: An Ammonium Dichromate Volcano: Change during a Chemical Reaction. The starting material is solid ammonium dichromate. A chemical reaction transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor (in addition, energy in the form of heat and light is released). During the reaction, the distribution of atoms changes, but the number of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced. Figure used with permission from Wikipedia. See video here:* https://www.youtube.com/watch?v=CW4hN0dYnkM

Chemical reactions are represented on paper by ***chemical equations***. For example, hydrogen gas (H_2) can react (burn) with oxygen gas (O_2) to form water (H_2O). The *chemical equation* for this *reaction* is written as:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \tag{1.1.1.1}$$

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 **1.1.1.1** is

$$\underbrace{(NH_4)_2Cr_2O_7}_{reactant} \rightarrow \underbrace{Cr_2O_3 + N_2 + 4\,H_2O}_{products} \tag{1.1.1.2}$$

The arrow is read as “yields” or “reacts to form.” Equation 1.1.1.2 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:

$$(NH_4)_2Cr_2O_7\,(s) \rightarrow Cr_2O_3\,(s) + N_2\,(g) + 4\,H_2O\,(g) \tag{1.1.1.3}$$

Equation 1.1.1.3 is identical to Equation 1.1.1.2 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 1.1.1.2 and 1.1.1.3. 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 1.1.1.2 and 1.1.1.3 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.

A chemical reaction changes only the distribution of atoms, not the number of atoms.

Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of n-heptane (C_7H_{16}), an important component of gasoline:

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$$\mathrm{C_7H_{16}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)} \tag{1.1.1.4}$$

The complete combustion of any hydrocarbon with sufficient oxygen always yields carbon dioxide and water.

Equation 1.1.1.4 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, the coefficients of the reactants and products must be adjusted to give the

same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure **1.1.1.3**.

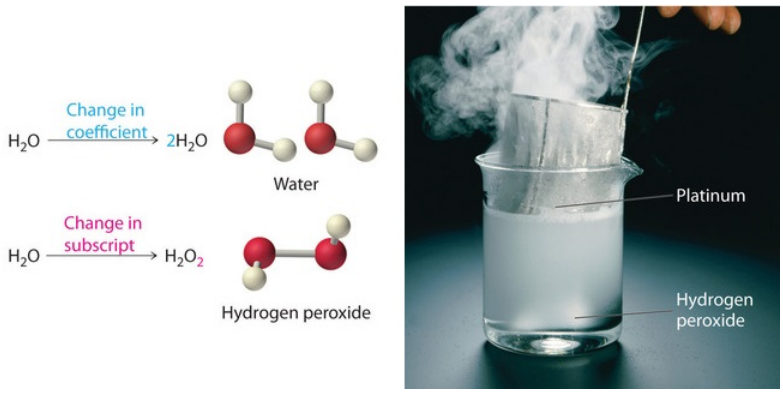


***Figure* 1.1.1.2:** *Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.*

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The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Check your work by counting the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example 1.1.1.1*A*: Combustion of Heptane

To demonstrate this approach, let's use the combustion of n-heptane (Equation 1.1.1.4) as an example.

1. **Identify the most complex substance**. The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients**. Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + H_2O \tag{1.1.1.5}$$

3. **Balance polyatomic ions as a unit**. There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms**. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H2O molecules, each of which contains 2 hydrogen atoms, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + 8\,H_2O \tag{1.1.1.6}$$

The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side:

$$C_7H_{16}\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g) \tag{1.1.1.7}$$

5. **Check your work**. The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start.

Example 1.1.1.1*B*: Combustion of Isooctane

Consider, for example, a similar reaction, the combustion of isooctane (C_8H_{18}). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

$$C_8H_{18}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g) \tag{1.1.1.8}$$

1. **Identify the most complex substance**. Begin the balancing process by assuming that the final balanced chemical equation contains a single molecule of isooctane.
2. **Adjust the coefficients**. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + H_2O \tag{1.1.1.9}$$

3. **Balance polyatomic ions as a unit**. This step does not apply to this equation.
4. **Balance the remaining atoms**. Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{1.1.1.10}$$

The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient (25/2) to balance the oxygen atoms:

$$C_8H_{18} + \tfrac{25}{2}\,O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{1.1.1.11}$$

Equation 1.1.1.11 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{1.1.1.12}$$

5. **Check your work**. The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.

Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example 1.1.1.1*C*: Hydroxyapatite

The reaction of the mineral hydroxyapatite ($\mathbf{Ca_5(PO_4)_3OH}$) with phosphoric acid and water gives $\mathbf{Ca(H_2PO_4)_2 \cdot H_2O}$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.

Given: reactants and product

Asked for: balanced chemical equation

Strategy:

A. Identify the product and the reactants and then write the unbalanced chemical equation.
B. Follow the steps for balancing a chemical equation.

Solution:

A We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem (recall that phosphoric acid is H_3PO_4). The initial (unbalanced) equation is as follows:

$$\mathbf{Ca_5(PO_4)_3OH\,(s) + H_3PO_4\,(aq) + H_2O_{(l)} \rightarrow Ca(H_2PO_4)_2 \cdot H_2O_{(s)}} \tag{1.1.1.13}$$

1. **B Identify the most complex substance**. We start by assuming that only one molecule or formula unit of the most complex substance, $\mathbf{Ca_5(PO_4)_3OH}$, appears in the balanced chemical equation.

2. **Adjust the coefficients**. Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $Ca_5(PO_4)_3(OH)$ contains 5 calcium atoms, so we need 5 $Ca(H_2PO_4)_2$•H_2O on the right side:

$$Ca_5(PO_4)_3OH + H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O \tag{1.1.1.14}$$

3. **Balance polyatomic ions as a unit**. It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion (PO_4^{3-}), shows up in three places. In H_3PO_4, the phosphate ion is combined with three H^+ ions to make phosphoric acid (H_3PO_4), whereas in $Ca(H_2PO_4)_2 \cdot H_2O$ it is combined with two H^+ ions to give the dihydrogen phosphate ion. Thus it is easier to balance PO_4 as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 PO_4 units on the right side but only 4 on the left. The simplest way to balance the PO_4 units is to place a coefficient of 7 in front of H_3PO_4:

$$Ca_5(PO_4)_3OH + 7\,H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O \tag{1.1.1.15}$$

Although OH^- is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

4. **Balance the remaining atoms**. We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, H_2O, by placing a coefficient of 4 in front of H_2O on the left side, giving a total of 4 H_2O molecules:

$$Ca_5(PO_4)_3OH\,(s) + 7\,H_3PO_4\,(aq) + 4\,H_2O\,(l) \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O\,(s) \tag{1.1.1.16}$$

The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 45 oxygen atoms on each side.

5. **Check your work**. Both sides of the equation contain 5 calcium atoms, 10 phosphorus atoms, 30 hydrogen atoms, and 45 oxygen atoms.

Exercise 1.1.1.1: Fermentation

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol (CH_3CH_2OH and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.

Answer

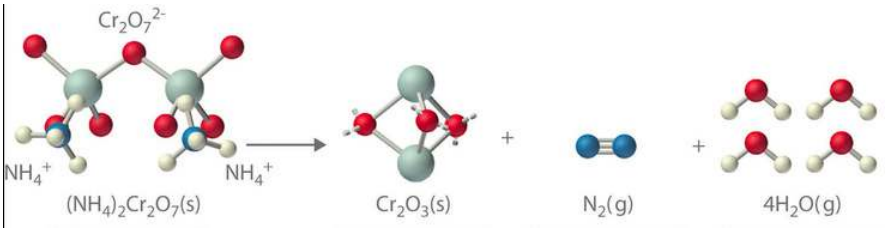
$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

Interpreting Chemical Equations (Part 1)

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides quantitative information. Specifically, it gives the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficient of that species (e.g., the 4 preceding H_2O in Equation 1.1.1.2). When no coefficient is written in front of a

species, the coefficient is assumed to be 1. As illustrated in Figure **1.1.1.4**, the coefficients allow Equation 1.1.1.2 to be interpreted in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One formula unit of $(NH_4)_2Cr_2O_7$ yields 1 formula unit of Cr_2O_3, 1 molecule of N_2, and 4 molecules of H_2O.



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Figure 1.1.1.4***:*** *The Balanced Chemical Reaction for the Ammonium Dichromate Volcano*

The chemical equation does not, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. These issues are considered in more detail in later chapters.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call combustion. Based on these experiments, he proposed that “Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal.” Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

Example 1.1.1.2: Combustion of Glucose

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l) \tag{1.1.1.17}$$

Construct a table showing how to interpret the information in this equation in terms of single molecule of glucose.

Strategy: Use the coefficients from the balanced chemical equation to determine the molecular ratios.

Solution: This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O.

Summary

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows

the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a balanced chemical equation, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species

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1.1.2: Some Simple Patterns of Chemical Reactivity

Learning Objectives

- To introduce the basic patterns of chemical reaction.

There is an underlying explanation of why a reaction takes place from an underlying chemical theory based on chemical reactivity. In this sections, we discussed various reactions to identify key chemical trends that allows chemists to predict the outcome of chemical reactions. By recognizing general patterns of chemical reactivity, you will be able to successfully predict the products formed by a given combination of reactants We can often predict a reaction if we have seen a similar reaction before. For example, sodium (Na) reacts with water (H_2O) to form sodium hydroxide ($NaOH$) and H_2 gas:

$$2\,\mathrm{Na(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{NaOH(aq)} + \mathrm{H_2(g)} \tag{1.1.2.1}$$

with (aq) indicating aqueous liquid. As discussed later, potassium (K) is in the same family (column) of elements as sodium and exhibits similar chemistry. Therefore, one might *predict* that the reaction of K with H_2O would be similar to that of Na:

$$2\,\mathrm{K(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{KOH(aq)} + \mathrm{H_2(g)} \tag{1.1.2.2}$$

In fact, all alkali metals react with water to form their hydroxide compounds and hydrogen.

Combination and Decomposition Reactions

In ***combination reactions,*** two or more compounds react to form a single, more complex compound. Many elements react with one another in this fashion to form compounds. The general chemical equation for combination reaction is:

$$A + B \rightarrow C \tag{1.1.2.3}$$

and an example includes the generation of ammonia (NH_3 from nitrogen (N_2 and hydrogen (H_2):

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightarrow 2\,\mathrm{NH_3(g)} \tag{1.1.2.4}$$

In ***decomposition reactions*** one substance undergoes a reaction to form two or more simpler products. Such reactions often occur when compounds are heated or electricity is added. The general chemical equation for decomposition reaction is:

$$A \rightarrow B + C \tag{1.1.2.5}$$

For example, the thermal decomposition of limestone ($CaCO_3$) generates quicklime (CaO) and carbon dioxide (CO_2)

$$\mathrm{CaCO_3(s)} \rightarrow \mathrm{CaO(s)} + \mathrm{CO_2(g)} \tag{1.1.2.6}$$

Combustion in Air

Combustion reactions are rapid reactions that produce a flame. Most common combustion reactions involve oxygen (O_2) from the air as a *reactant*. A common class of compounds which can participate in combustion reactions are *hydrocarbons* (compounds that contain only carbon and hydrogen).

When hydrocarbons are combusted they react with oxygen (O_2) to form carbon dioxide (CO_2) and water (H_2O). For example, when propane is burned the reaction is:

$$\mathrm{C_3H_8(g)} + 5\,\mathrm{O_2(g)} \rightarrow 3\,\mathrm{CO_2(g)} + 4\,\mathrm{H_2O(l)} \tag{1.1.2.7}$$

Other compounds which contain carbon, hydrogen and oxygen (e.g. the alcohol *methanol* CH_3OH, and the sugar *glucose* $C_6H_{12}O_6$) also combust in the presence of oxygen (O_2) to produce CO_2 and H_2O.

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1.1.3: Avogadro's Number and the Mole

Learning Objectives

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

Molecular and Formula Masses

The molecular mass of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example **1.1.3.1**.

Example 1.1.3.1: Molecular Mass of Ethanol

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

Given: molecule

Asked for: molecular mass

Strategy:

A. Determine the number of atoms of each element in the molecule.
B. Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.
C. Add together the masses to give the molecular mass.

Solution:

A The molecular formula of ethanol may be written in three different ways: $\mathbf{CH_3CH_2OH}$ (which illustrates the presence of an ethyl group, CH_3CH_{2-}, and an −OH group), $\mathbf{C_2CH_5OH}$, and $\mathbf{C_2H_6O}$; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

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

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

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

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

C Adding together the masses gives the molecular mass:

$$24.022\,amu + 6.0474\,amu + 15.9994\,amu = 46.069\,amu$$

Exercise 1.1.3.1: 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.

Example 1.1.3.2: 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

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

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

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

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

$$120.234\,amu + 61.947522\,amu + 127.9952\,amu = 310.177\,amu$$

Exercise 1.1.3.2: Formula Mass of Silicon Nitride

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

Answer

$140.29\,amu$

The Mole

Dalton's theory that each chemical compound has a particular combination of atoms and that the ratios of the numbers of atoms of the elements present are usually small whole numbers. It also describes the law of multiple proportions, which states that the ratios of the masses of elements that form a series of compounds are small whole numbers. The problem for Dalton and other early

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

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

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

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

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

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

Molar Mass

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

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

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

The molar mass of naturally-occurring carbon is different from that of carbon-12, and is not an integer because carbon occurs as a mixture of carbon-12, carbon-13, and carbon-14. One mole of carbon still has 6.022×10^{23} carbon atoms, but 98.89% of those atoms are carbon-12, 1.11% are carbon-13, and a trace (about 1 atom in 1012) are carbon-14. (For more information, see Section 1.6 "Isotopes and Atomic Masses".) Similarly, the molar mass of uranium is 238.03 g/mol, and the molar mass of iodine is 126.90 g/mol. When dealing with elements such as iodine and sulfur, which occur as a diatomic molecule (I_2) and a polyatomic molecule (S_8), respectively, molar mass usually refers to the mass of 1 mol of atoms of the element—in this case I and S, not to the mass of 1 mol of molecules of the element (I_2 and S_8).

The molar mass of ethanol is the mass of ethanol (C_2H_5OH) that contains 6.022×10^{23} ethanol molecules. As in Example **1.1.3.1**, the molecular mass of ethanol is 46.069 amu. Because 1 mol of ethanol contains 2 mol of carbon atoms (2 × 12.011 g), 6 mol of hydrogen atoms (6 × 1.0079 g), and 1 mol of oxygen atoms (1 × 15.9994 g), its molar mass is 46.069 g/mol. Similarly, the formula mass of calcium phosphate [$Ca_3(PO_4)_2$] is 310.177 amu, so its molar mass is 310.177 g/mol. This is the mass of calcium phosphate that contains 6.022×10^{23} formula units.

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

$$(moles)(molarmass) \rightarrow mass \tag{1.1.3.1}$$

or, more specifically,

$$moles\left(\frac{grams}{mole}\right) = grams \tag{1.1.3.2}$$

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

$$\left(\frac{grams}{molarmass}\right) \rightarrow moles \tag{1.1.3.3}$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles \tag{1.1.3.4}$$

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:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(l) \tag{1.1.3.5}$$

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?

$$(1.57\ mol\ O_2)\left(\frac{2\ mol\ H_2O}{1\ mol\ O_2}\right) = 3.14\ mol\ H_2O \tag{1.1.3.6}$$

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 1.1.3.3: Combustion of Butane

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

$$2\,C_4H_{10}\,(l) + 13\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 10\,H_2O\,(l) \tag{1.1.3.7}$$

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:

grams of reactant → moles of reactant → moles of product → grams of product

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

$$(1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right) = 1.72 \times 10^{-2}\ mol\ C_4H_{10} \tag{1.1.3.8}$$

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

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \tag{1.1.3.9}$$

Therefore:

$$\left(\frac{8\ mol\ CO_2}{2\ mol\ C_4H_{10}}\right) \times 1.72 \times 10^{-2}\ mol\ C_4H_{10} = 6.88 \times 10^{-2}\ mol\ CO_2 \tag{1.1.3.10}$$

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):

$$6.88 \times 10^{-2}\ mol\ CO_2\left(\frac{44.0\ g\ CO_2}{1\ mol\ CO_2}\right) = 3.03\ g\ CO_2 \tag{1.1.3.11}$$

Be sure to pay attention to the units when converting between mass and moles. Figure **1.1.3.1** 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 Examples **1.1.3.3** and **1.1.3.4**.

	MASS		Conversion factor		AMOUNT OF SUBSTANCE		Conversion factor		NUMBER OF PARTICLES
Units:	grams (g)	X	$\frac{1}{\text{molar mass (g/mol)}}$	=	moles (mol)	X	$\frac{\text{Avogadro's number of particles}}{1\ \text{mol}}$	=	atoms, molecules, formula units
Example:	10.00 ~~g C~~	X	$\frac{1\ \text{mol C}}{12.011\ \text{~~g C~~}}$	=	0.8326 ~~mol C~~	X	$\frac{6.022 \times 10^{23}\ \text{atoms C}}{1\ \text{~~mol C~~}}$	=	5.014×10^{23} atoms C

	NUMBER OF PARTICLES		Conversion factor		AMOUNT OF SUBSTANCE		Conversion factor		MASS
Units:	atoms, molecules, formula units	X	$\frac{1\ \text{mol}}{\text{Avogadro's number of particles}}$	=	moles (mol)	X	molar mass (g/mol)	=	grams (g)
Example:	5.014×10^{23} ~~atoms C~~	X	$\frac{1\ \text{mol C}}{6.022 \times 10^{23}\ \text{~~atoms C~~}}$	=	0.8326 ~~mol C~~	X	$\frac{12.011\ \text{g C}}{1\ \text{~~mol C~~}}$	=	10.00 g C

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Figure 1.1.3.1: A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

Example 1.1.3.4: Ethylene Glycol

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 The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 1.1.3.1: 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):

$$\frac{\text{mass of ethylene glycol (g)}}{\text{molar mass (g/mol)}} = \text{moles ethylene glycol (mol)} \tag{1.1.3.12}$$

So

$$35.00\,g\text{ethylene glycol}\left(\frac{1\,mole\text{ethylene glycol}}{62.068\,g\text{ethylene glycol}}\right) = 0.5639\,mol\text{ethylene glycol} \tag{1.1.3.13}$$

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.

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

$$\text{molecules of ethylene glycol} = 0.5639\,mol\left(\frac{6.022\times10^{23}\,molecules}{1\,mol}\right) \tag{1.1.3.14}$$

$$= 3.396\times10^{23}\,molecules \tag{1.1.3.15}$$

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.

Exercise 1.1.3.4: Freon-11

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

a. moles.
b. molecules.

Answer a

0.546 mol

Answer b

3.29×10^{23} molecules

Example 1.1.3.5

Calculate the mass of 1.75 mol of each compound.

a. $\mathbf{S_2Cl_2}$ (common name: sulfur monochloride; systematic name: disulfur dichloride)
b. $\mathbf{Ca(ClO)_2}$ (calcium hypochlorite)

Given: number of moles and molecular or empirical formula

Asked for: mass

Strategy:

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

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

Solution:

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

A The molar mass of $\mathbf{S_2Cl_2}$ is 135.036 g/mol.

B The mass of 1.75 mol of $\mathbf{S_2Cl_2}$ is calculated as follows:

$$moles S_2Cl_2 \left[\text{molar mass}\left(\frac{g}{mol}\right)\right] \rightarrow mass of S_2Cl_2\,(g) \tag{1.1.3.16}$$

$$1.75\,mol S_2Cl_2 \left(\frac{135.036\,g S_2Cl_2}{1\,mol S_2Cl_2}\right) = 236\,g S_2Cl_2 \tag{1.1.3.17}$$

A 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:

$$moles Ca(ClO)_2 \left[\frac{\text{molar mass} Ca(ClO)_2}{1\,mol Ca(ClO)_2}\right] = mass Ca(ClO)_2 \tag{1.1.3.18}$$

$$1.75\,mol Ca(ClO)_2 \left[\frac{142.983\,g Ca(ClO)_2}{1\,mol Ca(ClO)_2}\right] = 250\,g Ca(ClO)_2 \tag{1.1.3.19}$$

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 1.1.3.5

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

Answer 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:

$$\mathbf{2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(l)}$$

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?

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

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 1.1.3.6

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

$$2\,C_4H_{10}\,(l) + 13\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 10\,H_2O\,(l)$$

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:

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

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

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

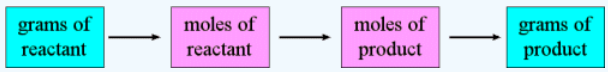
Therefore:

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

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):

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

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.

Interpreting Chemical Equations (Part 2)

Previously, we discussed that chemical equations give the relative amounts of reactants and products consumed or produced in a reaction. This was discussed in terms of the the number of atoms, molecules, or formula units of a reactant or a product. A chemical equation can also be interpreted interms of moles of a reactant or product. As illustrated below, the coefficients allow interpreted in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of Cr_2O_3, 1 mol of N_2, and 4 mol of H_2O.

- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of Cr_2O_3, 28 g of N_2, and 72 g of H_2O.
- A total of 6.022×10^{23} formula units of $(NH_4)_2Cr_2O_7$ yields 6.022×10^{23} formula units of Cr_2O_3, 6.022×10^{23} molecules of N_2, and 24.09×10^{23} molecules of H_2O.

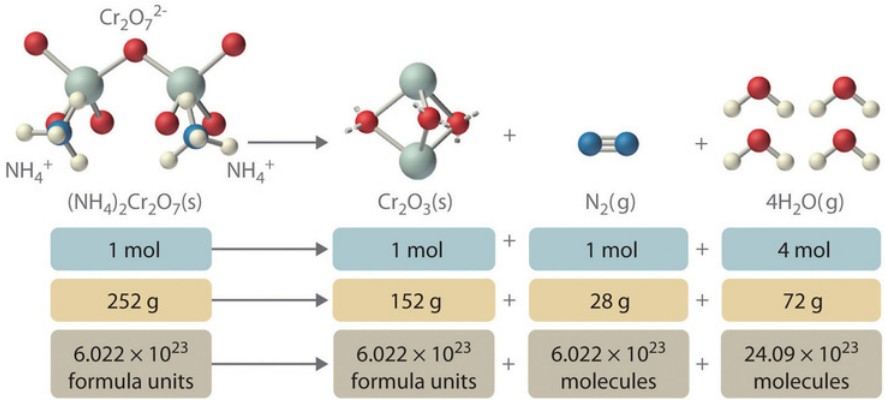


Figure **1.1.3.4**: The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano

These are all chemically equivalent ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratio. For example, the mole ratio of H_2O to N_2 in Equation ??? is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass:

$$252\ g\ \text{of}\ (NH_4)_2Cr_2O_7 \tag{1.1.3.20}$$

yield

$$152 + 28 + 72 = 252\ g\ \text{of products.} \tag{1.1.3.21}$$

The chemical equation does not, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. These issues are considered in more detail in later chapters.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call combustion. Based on these experiments, he proposed that "Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal." Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

Example 1.1.3.2: Combustion of Glucose

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l) \tag{1.1.3.22}$$

Construct a table showing how to interpret the information in this equation in terms of

a. a single molecule of glucose.
b. moles of reactants and products.
c. grams of reactants and products represented by 1 mol of glucose.
d. numbers of molecules of reactants and products represented by 1 mol of glucose.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

A. Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.
B. Use the molar masses of the reactants and products to convert from moles to grams.
C. Use Avogadro's number to convert from moles to the number of molecules.

Solution:

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

a. One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O.
b. One mole of glucose reacts with 6 mol of O_2 to yield 6 mol of CO_2 and 6 mol of H_2O.
c. To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; O_2, 31.9988; CO_2, 44.010; and H_2O, 18.015.

$$\textbf{mass of reactants} = \textbf{mass of products}$$

$$g\,glucose + g\,O_2 = g\,CO_2 + g\,H_2O$$

$$1\,mol\,glucose\left(\frac{180.16\,g}{1\,mol\,glucose}\right) + 6\,mol\,O_2\left(\frac{31.9988\,g}{1\,mol\,O_2}\right) \tag{1.1.3.23}$$

$$= 6\,mol\,CO_2\left(\frac{44.010\,g}{1\,mol\,CO_2}\right) + 6\,mol\,H_2O\left(\frac{18.015\,g}{1\,mol\,H_2O}\right) \tag{1.1.3.24}$$

$$372.15\,g = 372.15\,g \tag{1.1.3.25}$$

C One mole of glucose contains Avogadro's number (6.022×10^{23}) of glucose molecules. Thus 6.022×10^{23} glucose molecules react with ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} oxygen molecules to yield ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} molecules each of CO_2 and H_2O.

In tabular form:

	$C_6H_{12}O_{6\,(s)}$	+	$6O_{2\,(g)}$	→	$6CO_{2\,(g)}$		$6H_2O_{(l)}$
a.	1 molecule		6 molecules		6 molecules		6 molecules
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022×10^{23} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules		3.613×10^{24} molecule

Exercise 1.1.3.2: Ammonium Nitrate Explosion

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas. The explosion resulted from the following reaction:

$$2NH_4NO_{3\,(s)} \rightarrow 2N_{2\,(g)} + 4H_2O_{(g)} + O_{2\,(g)} \tag{1.1.3.26}$$

Construct a table showing how to interpret the information in the equation in terms of

a. individual molecules and ions.
b. moles of reactants and products.
c. grams of reactants and products given 2 mol of ammonium nitrate.
d. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

Answer:

	$2NH_4NO_{3\,(s)}$	→	$2N_{2\,(g)}$	+	$4H_2O_{(g)}$	+	$O_{2\,(g)}$
a.	$2NH_4^+$ ions and $2NO_3^-$ ions		2 molecules		4 molecules		1 molecule
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules

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.

1.1.3: Avogadro's Number and the Mole is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

1.1.4: Empirical and Molecular Formulas

Learning Objectives

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

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

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:

$$1 \times (12.011\ amu) + 4 \times (1.008) = 16.043\ amu \tag{1.1.4.1}$$

the relative (mass) percentages of carbon and hydrogen are

$$\%C = \frac{1 \times (12.011\ amu)}{16.043 amu} = 0.749 = 74.9\% \tag{1.1.4.2}$$

$$\%H = \frac{4 \times (1.008\ amu)}{16.043\ amu} = 0.251 = 25.1\% \tag{1.1.4.3}$$

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:

$$\text{mass of C/mol of sucrose} = 12\,mol\,C \times \frac{12.011\,g\,C}{1\,mol\,C} = 144.132\,g\,C \tag{1.1.4.4}$$

$$\text{mass of H/mol of sucrose} = 22\,mol\,H \times \frac{1.008\,g\,H}{1\,mol\,H} = 22.176\,g\,C \tag{1.1.4.5}$$

$$\text{mass of O/mol of sucrose} = 11\,mol\,O \times \frac{15.999\,g\,O}{1\,mol\,O} = 175.989\,g\,O \tag{1.1.4.6}$$

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:

$$\text{mass } = \frac{\text{mass of C/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{144.132\,g\,C}{342.297\,g/mol} \times 100 = 42.12\% \tag{1.1.4.7}$$

$$\text{mass } = \frac{\text{mass of H/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{22.176\,g\,H}{342.297\,g/mol} \times 100 = 6.48\% \tag{1.1.4.8}$$

$$\text{mass} = \frac{\text{mass of O/mol sucrose}}{\text{molar mass of sucrose}} \times 100 = \frac{175.989\,g\,O}{342.297\,g/mol} \times 100 = 51.41\% \tag{1.1.4.9}$$

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

$$42.12\% + 6.48\% + 51.41\% = 100.01\% \tag{1.1.4.10}$$

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.

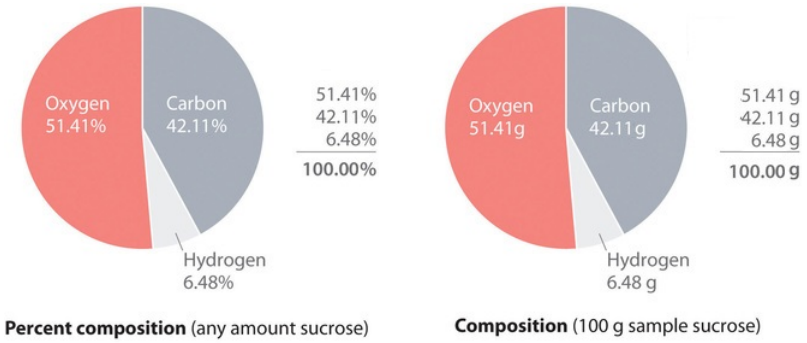
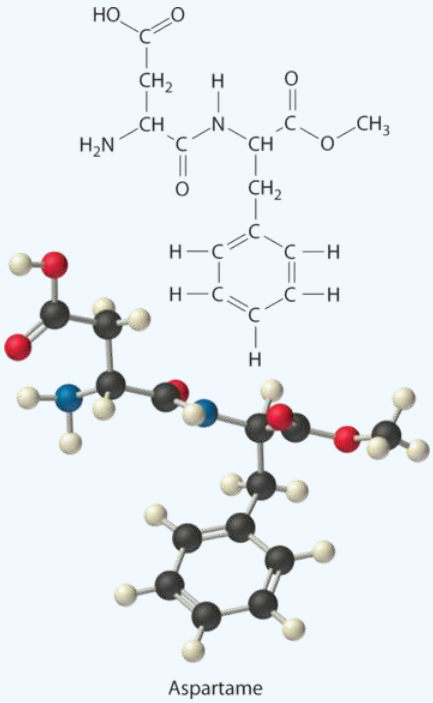


Figure 1.1.4.1: Percent and absolute composition of sucrose

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 1.1.4.1: NutraSweet

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



Aspartame

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:

$$C_{14}H_{18}N_2O_5 \text{molar mass of aspartame} = 294.277\,g/mol \tag{1.1.4.11}$$

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:

$$mass\%\,C = \frac{168.154\,g\,C}{294.277\,g\,aspartame} \times 100 = 57.14\%C \tag{1.1.4.12}$$

$$mass\%\,H = \frac{18.114\,g\,H}{294.277\,g\,aspartame} \times 100 = 6.16\%H \tag{1.1.4.13}$$

$$mass\%\,N = \frac{28.014\,g\,N}{294.277\,g\,aspartame} \times 100 = 9.52\% \tag{1.1.4.14}$$

$$mass\%\,O = \frac{79.995\,g\,O}{294.277\,g\,aspartame} \times 100 = 27.18\% \tag{1.1.4.15}$$

As a check, we can add the percentages together:

$$57.14\% + 6.16\% + 9.52\% + 27.18\% = 100.00\% \tag{1.1.4.16}$$

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:

$$\text{mass of C} = 1.00\,g\,aspartame \times \frac{57.14\,g\,C}{100\,g\,aspartame} = 0.571\,g\,C \tag{1.1.4.17}$$

Exercise 1.1.4.1: 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

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 **1.1.4.2**), 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 **1.1.4.2**), Fleming called the active ingredient in the broth penicillin.

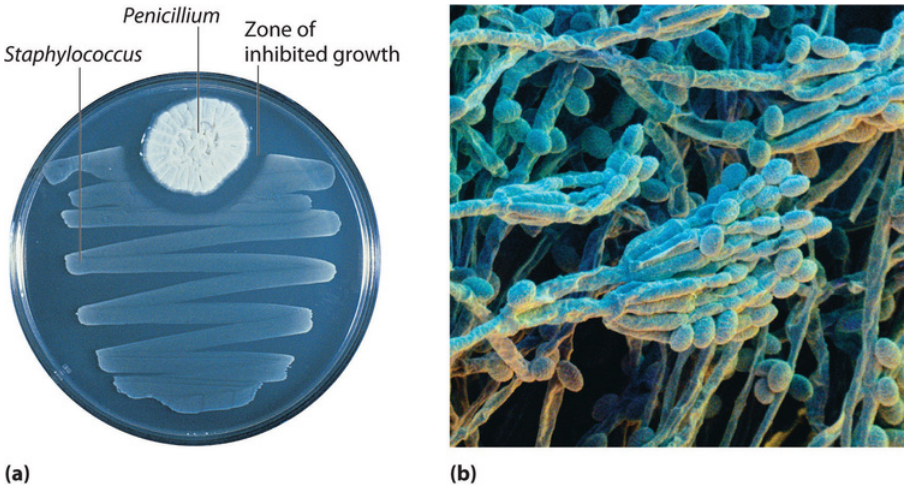


Figure **1.1.4.2**: Penicillium. (a) Penicillium mold is growing in a culture dish; the photo shows its effect on bacterial growth. (b) In this photomicrograph of Penicillium, its rod- and pencil-shaped branches are visible. The name comes from the Latin penicillus, meaning “paintbrush.”

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:

$$\frac{mass\,(g)}{molar\ mass\ (g/mol)} = (g)\left(\frac{mol}{g}\right) = mol \tag{1.1.4.18}$$

$$53.9\,g\,C\left(\frac{1\,mol\,C}{12.011\,g\,C}\right) = 4.49\,mol\,C \tag{1.1.4.19}$$

$$4.8\,g\,H\left(\frac{1\,mol\,H}{1.008g\,H}\right) = 4.8\,mol\,H \tag{1.1.4.20}$$

$$7.9\,g\,N\left(\frac{1\,mol\,N}{14.007\,g\,N}\right) = 0.56\,mol\,N \tag{1.1.4.21}$$

$$9\,g\,S\left(\frac{1\,mol\,S}{32.065\,g\,S}\right) = 0.28\,mol\,S \tag{1.1.4.22}$$

$$6.5\,g\,Na\left(\frac{1\,mol\,Na}{22.990\,g\,Na}\right) = 0.28\,mol\,Na \tag{1.1.4.23}$$

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:

$$C: \frac{4.49}{0.28} = 16 \quad H: \frac{4.8}{0.28} = 17 \quad N: \frac{0.56}{0.28} = 2.0 \tag{1.1.4.24}$$

$$S: \frac{0.28}{0.28} = 1.0 \quad Na: \frac{0.28}{0.28} = 1.0 \quad O: \frac{1.12}{0.28} = 4.0 \tag{1.1.4.25}$$

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 **1.1.4.3**) was not determined until 1948.

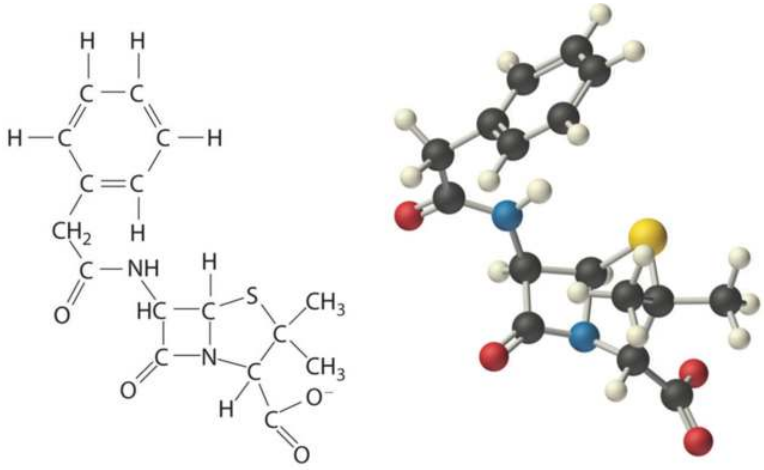


Figure **1.1.4.3**: Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G

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 1.1.4.2: 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:

$$\text{moles Ca} = 38.77\,g\,Ca \times \frac{1\,mol\,Ca}{40.078\,g\,Ca} = 0.9674\,mol\,Ca \tag{1.1.4.26}$$

$$\text{moles P} = 19.97\,g\,P \times \frac{1\,mol\,P}{30.9738\,g\,P} = 0.6447\,mol\,Ca \tag{1.1.4.27}$$

$$\text{moles O} = 41.27\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 2.5800\,mol\,O \tag{1.1.4.28}$$

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:

$$P: \frac{0.6447\,mol\,P}{0.6447\,mol\,P} = 1.000 \quad Ca: \frac{0.9674}{0.6447} = 1.501 \quad O: \frac{2.5800}{0.6447} = 4.002 \tag{1.1.4.29}$$

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 "Molecules, Ions, and Chemical Formulas" 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 1.1.4.2: Ammonium Nitrate

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.

Answer

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

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 **1.1.4.3**).

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:

$$moles\,C = 39.68\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 3.304\,mol\,C \tag{1.1.4.30}$$

$$moles\,H = 6.58\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 6.53\,mol\,H \tag{1.1.4.31}$$

$$moles\,O = 53.79\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 3.362\,mol\,O \tag{1.1.4.32}$$

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:

$$C: \frac{3.304}{3.304} = 1.000 \quad H: \frac{6.53}{3.304} = 1.98 \quad O: \frac{3.362}{3.304} = 1.018 \tag{1.1.4.33}$$

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,

$$\begin{aligned}\text{formula mass of}CH_2O = &\left[1\,molC\left(\frac{12.011\,g}{1\,mol\,C}\right)\right] + \left[2\,mol\,H\left(\frac{1.0079\,g}{1\,mol\,H}\right)\right] \\ &+ \left[1\,mole\,O\left(\frac{15.5994\,mol\,O}{1\,mol\,O}\right)\right] = 30.026g\end{aligned} \tag{1.1.4.34}$$

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:

$$n = \frac{180\,g}{30.026\,g/CH_2O} = 5.99 \approx 6CH_2O\,\text{formula units} \tag{1.1.4.35}$$

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 **1.1.4.4**.

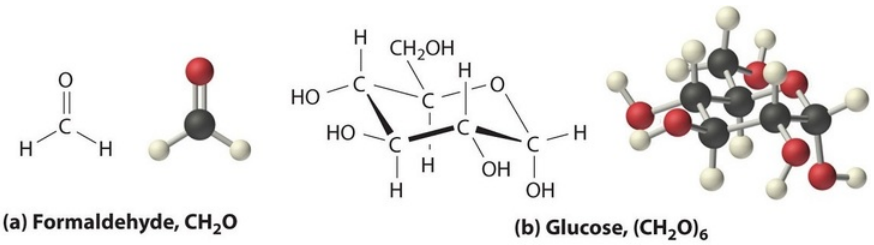


Figure 1.1.4.4: Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose

Example 1.1.4.3: 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.

$$moles\,C = 49.18\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 4.095\,mol\,C \tag{1.1.4.36}$$

$$moles\,H = 5.39\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 5.35\,mol\,H \tag{1.1.4.37}$$

$$moles\,N = 28.65\,g\,N \times \frac{1\,mol\,N}{14.0067\,g\,N} = 2.045\,mol\,N \tag{1.1.4.38}$$

$$moles\,O = 16.68\,g\,O \times \frac{1\,mol\,O}{15.9994\,g\,O} = 1.043\,mol\,O \tag{1.1.4.39}$$

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:

$$O: \frac{1.043}{1.043} = 1.000 \quad C: \frac{4.095}{1.043} = 3.926 \quad H: \frac{5.35}{1.043} = 5.13 \quad N: \frac{2.045}{1.043} = 1.960 \tag{1.1.4.40}$$

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:

$$4C \quad (4\,atoms\,C)(12.011\,g/atom\,C) = 48.044\,g \tag{1.1.4.41}$$

$$5H \quad (5\,atoms\,H)(1.0079\,g/atom\,H) = 5.0395\,g \tag{1.1.4.42}$$

$$2N \quad (2\,atoms\,N)(14.0067\,g/atom\,N) = 28.0134\,g \tag{1.1.4.43}$$

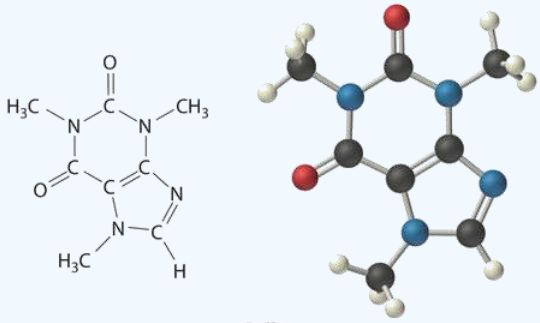
$$+1O \quad (1\,atom\,O)(15.9994\,g/atom\,O) = 15.9994\,g \tag{1.1.4.44}$$

$$C_4H_5N_2O \quad \text{formula mass of caffeine} = 97.096\,g \tag{1.1.4.45}$$

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

$$\frac{196 g/mol}{97.096 g/C_4H_5N_2O} = 2.02 \approx 2\,C_4H_5N_2O\,\text{empirical formula units} \tag{1.1.4.46}$$

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:



Caffeine

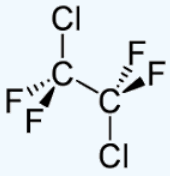
Exercise 1.1.4.3: Freon-114

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

$$C_2Cl_2F_4$$



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.

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1.1.5: Empirical Formulas from Analysis

Learning Objectives

- To understand the definition and difference between empirical formulas and molecular formulas
- To understand how combustion analysis can be used to identify molecular formulas

Molecular formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's molecular formula cannot be reduced any more, then the empirical formula is the same as the molecular formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the molecular formula (other techniques can though). Once known, the molecular formula can be calculated from the empirical formula.

Molecular Formula from Empirical Formula

The chemical formula for a compound obtained by composition analysis is always the empirical formula. We can obtain the chemical formula from the empirical formula if we know the molecular weight of the compound. The chemical formula will always be some *integer multiple* of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula). The general flow for this approach is shown in Figure **1.1.5.1** and demonstrated in Example **1.1.5.2**.

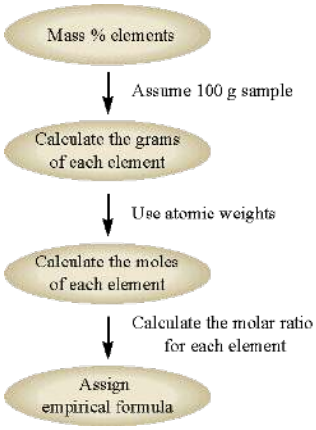


Figure 1.1.5.1: The general flow chart for solving empirical formulas from known mass percentages.

Example 1.1.5.1: Ascorbic Acid

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What is the empirical and chemical formula for ascorbic acid?

Solution

Consider an arbitrary amount of 100 grams of ascorbic acid, so we would have:

- 40.92 grams C
- 4.58 grams H
- 54.50 grams O

This would give us how many moles of each element?

- Carbon

$$(40.92\ \cancel{g\,C}) \times \left(\frac{1\ mol\ C}{12.011\ \cancel{g\,C}} \right) = 3.407\ mol\ C \tag{1.1.5.1}$$

- Hydrogen

$$(4.58\ \cancel{g\ H}) \times \left(\frac{1\ mol\ H}{1.008\ \cancel{g\ H}} \right) = 4.544\ mol\ H \tag{1.1.5.2}$$

- Oxygen

$$(54.50\ \cancel{g\ O}) \times \left(\frac{1\ mol\ O}{15.999\ \cancel{g\ O}} \right) = 3.406\ mol\ O \tag{1.1.5.3}$$

Determine the simplest whole number ratio by dividing by the smallest molar amount (3.406 moles in this case - see oxygen):

- Carbon

$$C = \frac{3.407\ mol}{3.406\ mol} \approx 1.0 \tag{1.1.5.4}$$

- Hydrogen

$$C = \frac{4.5.44\ mol}{3.406\ mol} = 1.0 \tag{1.1.5.5}$$

- Oxygen

$$C = \frac{3.406\ mol}{3.406\ mol} = 1.0 \tag{1.1.5.6}$$

The relative molar amounts of carbon and oxygen appear to be equal, but the relative molar amount of hydrogen is higher. Since we cannot have "fractional" atoms in a compound, we need to normalize the relative amount of hydrogen to be equal to an integer. 1.333 would appear to be 1 and 1/3, so if we multiply the relative amounts of each atom by '3', we should be able to get integer values for each atom.

C = (1.0)*3 = 3

H = (1.333)*3 = 4

O = (1.0)*3 = 3

or

$C_3H_4O_3$

This is our ***empirical formula*** for ascorbic acid.

What about the chemical formula? We are told that the experimentally determined molecular mass is **176 *amu***. What is the molecular mass of our empirical formula?

(3*12.011) + (4*1.008) + (3*15.999) = 88.062 *amu*

The molecular mass from our empirical formula is significantly lower than the experimentally determined value. What is the ratio between the two values?

(176 *amu*/88.062 *amu*) = 2.0

Thus, it would appear that our empirical formula is essentially one half the mass of the actual molecular mass. If we multiplied our empirical formula by '2', then the molecular mass would be correct. Thus, the actual molecular formula is:

2* $C_3H_4O_3$ = **$C_6H_8O_6$**

Combustion Analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure **1.1.5.2**). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

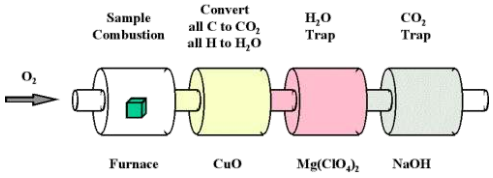


Figure* 1.1.5.2*: *Combustion analysis apparatus*

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 1.1.5.3 and a typical combustion analysis is illustrated in Examples 1.1.5.3 and 1.1.5.4.

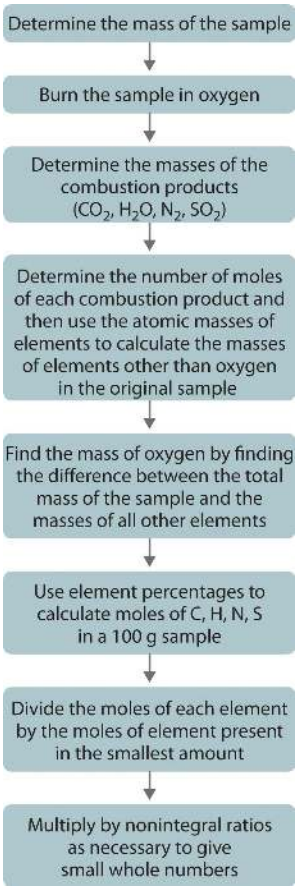


Figure 1.1.5.3: Steps for Obtaining an Empirical Formula from Combustion Analysis

Example 1.1.5.2: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561\ \cancel{g\ CO_2})\left(\frac{1\ mol\ CO_2}{44.0\ \cancel{g\ CO_2}}\right) = 0.0128\ mol\ CO_2 \tag{1.1.5.7}$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128 \ \cancel{mol\ C}) \left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}} \right) = 0.154\ g\ C \tag{1.1.5.8}$$

How about the hydrogen?

$$(0.306 \ \cancel{g\ H_2O}) \left(\frac{1\ mol\ H_2O}{18.0\ \cancel{g\ H_2O}} \right) = 0.017\ mol\ H_2O \tag{1.1.5.9}$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067 \ \cancel{g\ O}) \left(\frac{1\ mol\ O}{15.994\ \cancel{g\ O}} \right) = 0.0042\ mol\ O \tag{1.1.5.10}$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

Example 1.1.5.3: Combustion of Naphalene

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:

$$\underset{mass\ of\ C}{} = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,molC}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C} \tag{1.1.5.11}$$

$$= 1.883 \times 10^{-2}\,g\,C \tag{1.1.5.12}$$

$$\underset{mass\ of\ H}{} = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H} \tag{1.1.5.13}$$

$$= 1.264 \times 10^{-3}\,g\,H \tag{1.1.5.14}$$

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:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC \tag{1.1.5.15}$$

$$moles\,H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\,molH \tag{1.1.5.16}$$

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

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250 \tag{1.1.5.17}$$

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.

Exercises 1.1.5.1

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?

c. Formaldehyde is unstable as a pure gas, readily forming a mixture of a substance called trioxane and a polymer called paraformaldehyde. That is why formaldehyde is dissolved in a solvent, such as water, before it is sold and used. The molecular formula of trioxane, which contains carbon, hydrogen, and oxygen, can be determined using the data from two different experiments. In the first experiment, 17.471 g of trioxane is burned in the apparatus shown above, and 10.477 g H_2O and 25.612 g CO_2 are formed. In the second experiment, the molecular mass of trioxane is found to be 90.079. Determine the empirical and molecular formulas for tioxane.

d. Dianabol is one of the anabolic steroids that has been used by some athletes to increase the size and strength of their muscles. It is similar to the male hormone testosterone. Some studies indicate that the desired effects of the drug are minimal, and the side effects, which include sterility and increased risk of liver cancer and heart disease, keep most people from using it. The molecular formula of Dianabol, which consists of carbon, hydrogen, and oxygen, can be determined using the data from two different experiments. In the first experiment, 14.765 g of Dianabol is burned, and 43.257 g CO2 and 12.395 g H2O are formed. In the second experiment, the molecular mass of Dianabol is found to be 300.44. What is the molecular formula for Dianabol?

Answer a

The empirical formula is C_4H_5.

Answer b

33.81 mg of CO_2; 6.92 mg of H_2O

Answer c

The empirical formula is CH_2O. The molecular formula is $C_3H_6O_3$.

Answer d

The empirical formula is $C_{10}H_{14}O$. The molecular formula is $C_{20}H_{28}O_2$.

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1.1.6: Reaction Stoichiometry

Learning Objectives

- To balance equations that describe reactions in solution.
- To calculate the quantities of compounds produced or consumed in a chemical reaction.
- To solve quantitative problems involving the stoichiometry of reactions in solution.

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced. **Stoichiometry** is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. **A stoichiometric quantity** is the amount of product or reactant specified by the coefficients in a balanced chemical equation. This section describes how to use the stoichiometry of a reaction to answer questions like the following: How much oxygen is needed to ensure complete combustion of a given amount of isooctane? (This information is crucial to the design of nonpolluting and efficient automobile engines.) How many grams of pure gold can be obtained from a ton of low-grade gold ore? (The answer determines whether the ore deposit is worth mining.) If an industrial plant must produce a certain number of tons of sulfuric acid per week, how much elemental sulfur must arrive by rail each week?

All these questions can be answered using the concepts of the mole, molar and formula masses, and solution concentrations, along with the coefficients in the appropriate balanced chemical equation.

Stoichiometry Problems

When carrying out a reaction in either an industrial setting or a laboratory, it is easier to work with masses of substances than with the numbers of molecules or moles. The general method for converting from the mass of any reactant or product to the mass of any other reactant or product using a balanced chemical equation is outlined in and described in the following text.

Steps in Converting between Masses of Reactant and Product

1. Convert the mass of one substance (substance A) to the corresponding number of moles using its molar mass.
2. From the balanced chemical equation, obtain the number of moles of another substance (B) from the number of moles of substance A using the appropriate mole ratio (the ratio of their coefficients).
3. Convert the number of moles of substance B to mass using its molar mass. It is important to remember that some species are present in excess by virtue of the reaction conditions. For example, if a substance reacts with the oxygen in air, then oxygen is in obvious (but unstated) excess.

Converting amounts of substances to moles—and vice versa—is the key to all stoichiometry problems, whether the amounts are given in units of mass (grams or kilograms), weight (pounds or tons), or volume (liters or gallons).

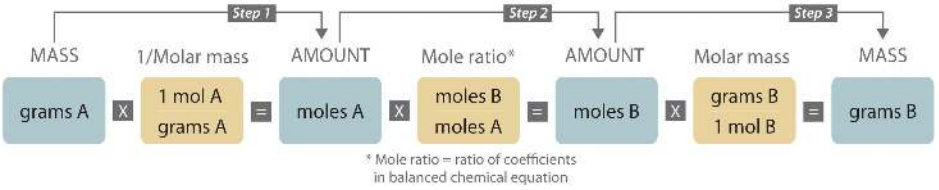


Figure **1.1.6.1**: A Flowchart for Stoichiometric Calculations Involving Pure Substances. The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.

To illustrate this procedure, consider the combustion of glucose. Glucose reacts with oxygen to produce carbon dioxide and water:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{3.6.1}$$

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 above can be adapted as follows:

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:

$$mass\ of\ CO_2 = 1.51\ mol\ CO_2 \times \frac{44.010\ g\ CO_2}{1\ mol\ CO_2} = 66.5\ g\ CO_2 \tag{1.1.6.1}$$

These operations can be summarized as follows:

$$45.3\ g\ glucose \times \frac{1\ mol\ glucose}{180.2\ g\ glucose} \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \times \frac{44.010\ g\ CO_2}{1\ mol\ CO_2} = 66.4\ g\ CO_2 \tag{1.1.6.2}$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. (Remember that you should generally carry extra significant digits through a multistep calculation to the end to avoid this!) 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 **1.1.6.1**, the mass of one reactant that is required to consume a given mass of another reactant.

Example 1.1.6.1: The US Space Shuttle

The combustion of hydrogen with oxygen to produce gaseous water is extremely vigorous, producing one of the hottest flames known. Because so much energy is released for a given mass of hydrogen or oxygen, this reaction was used to fuel the NASA (National Aeronautics and Space Administration) space shuttles, which have recently been retired from service. NASA engineers calculated the exact amount of each reactant needed for the flight to make sure that the shuttles did not carry excess fuel into orbit. Calculate how many tons of hydrogen a space shuttle needed to carry for each 1.00 tn of oxygen (1 tn = 2000 lb).

Given: reactants, products, and mass of one reactant

Asked for: mass of other reactant

Strategy:

A. Write the balanced chemical equation for the reaction.
B. Convert mass of oxygen to moles. From the mole ratio in the balanced chemical equation, determine the number of moles of hydrogen required. Then convert the moles of hydrogen to the equivalent mass in tons.

Solution:

We use the same general strategy for solving stoichiometric calculations as in the preceding example. Because the amount of oxygen is given in tons rather than grams, however, we also need to convert tons to units of mass in grams. Another conversion is needed at the end to report the final answer in tons.

A. We first use the information given to write a balanced chemical equation. Because we know the identity of both the reactants and the product, we can write the reaction as follows:

$$H_2(g) + O_2(g) \rightarrow H_2O(g) \tag{1.1.6.3}$$

This equation is not balanced because there are two oxygen atoms on the left side and only one on the right. Assigning a coefficient of 2 to both H_2O and H_2 gives the balanced chemical equation:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \tag{1.1.6.4}$$

Thus 2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O.

B.

1. To convert tons of oxygen to units of mass in grams, we multiply by the appropriate conversion factors:

$$mass\ of\ O_2 = 1.00\,tn \times \frac{2000\,lb}{tn} \times \frac{453.6\,g}{lb} = 9.07 \times 10^5\,g\,O_2 \tag{1.1.6.5}$$

2. Using the molar mass of O2 (32.00 g/mol, to four significant figures), we can calculate the number of moles of O2 contained in this mass of O2:

$$mol\,O_2 = 9.07 \times 10^5\,g\,O_2 \times \frac{1\,mol\,O_2}{32.00\,g\,O_2} = 2.83 \times 10^4\,mol\,O_2 \tag{1.1.6.6}$$

3. Now use the coefficients in the balanced chemical equation to obtain the number of moles of H2 needed to react with this number of moles of O2:BREAK

$$mol\,H_2 = mol\,O_2 \times \frac{2\,mol\,H_2}{1\,mol\,O_2} \tag{1.1.6.7}$$

$$= 2.83 \times 10^4\,mol\,O_2 \times \frac{2\,mol\,H_2}{1\,mol\,O_2} = 5.66 \times 10^4\,mol\,H_2 \tag{1.1.6.8}$$

4. The molar mass of H2 (2.016 g/mol) allows us to calculate the corresponding mass of H2:B

$$mass\ of\ H_2 = 5.66 \times 10^4\,mol\,H_2 \times \frac{2.016\,g\,H_2}{mol\,H_2} = 1.14 \times 10^5\,g\,H_2 \tag{1.1.6.9}$$

5. Finally, convert the mass of H2 to the desired units (tons) by using the appropriate conversion factors:

$$tons\,H_2 = 1.14 \times 10^5\,g\,H_2 \times \frac{1\,lb}{453.6\,g} \times \frac{1\,tn}{2000\,lb} = 0.126\,tn\,H_2 \tag{1.1.6.10}$$

The space shuttle had to be designed to carry 0.126 tn of H_2 for each 1.00 tn of O_2. Even though 2 mol of H_2 are needed to react with each mole of O_2, the molar mass of H2 is so much smaller than that of O_2 that only a relatively small mass of H_2 is needed compared to the mass of O_2.

Exercise 1.1.6.1: Roasting Cinnabar

Cinnabar, (or Cinnabarite) HgS is the common ore of mercury. Because of its mercury content, cinnabar can be toxic to human beings; however, because of its red color, it has also been used since ancient times as a pigment. Alchemists produced elemental mercury by roasting cinnabar ore in air:

$$HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g) \tag{1.1.6.11}$$

The volatility and toxicity of mercury make this a hazardous procedure, which likely shortened the life span of many alchemists. Given 100 g of cinnabar, how much elemental mercury can be produced from this reaction?

Answer

86.2 g

Exercise1.1.6.2: Copper Reacts with Nitric Acid

Copper reacts with nitric acid as follows:

$$\mathrm{Cu + 4\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O} \tag{1.1.6.12}$$

A chemist mixes 4.523 g of copper and 11.716 g of nitric acid.

a) Which reactant (if any) will remain if the reaction goes to completion, and how many grams of that reactant will be left over?

b) What mass of nitrogen dioxide will be formed, assuming 100% yield?

c) If the chemist isolates 8.333 g of copper(II) nitrate, what is the percent yield in this experiment?

Answer

a) First, you must determine the limiting reactant, which can be done in several ways. One simple option is to calculate the mass of one of the products based on each reactant; the reactant that gives the smaller mass of product is the limiting reactant. This method is convenient here because if we choose NO_2 as our product, we will also get the answer to part b of the problem.

If we use all of the Cu, we will form…

$$4.523\text{gCu} \times \frac{1\text{molCu}}{63.55\text{gCu}} \times \frac{2\text{mol}NO_2}{1\text{molCu}} \times \frac{46.01\text{g}NO_2}{1\text{mol}NO_2} = 6.549\text{g}NO_2 \tag{1.1.6.13}$$

If we use all of the HNO_3, we will form…

$$11.716\text{g}HNO_3 \times \frac{1\text{mol}HNO_3}{63.018\text{g}HNO_3} \times \frac{2\text{mol}NO_2}{4\text{mol}HNO_3} \times \frac{46.01\text{g}NO_2}{1\text{mol}NO_2} = 4.277\text{g}NO_2 \tag{1.1.6.14}$$

Since the HNO_3 gives less product, HNO_3 is the limiting reactant and will be completely consumed in the reaction. Therefore, **Cu will remain after the reaction goes to completion.** To calculate the remaining mass of Cu, we must first determine how much Cu is consumed, given that all of the HNO_3 reacts:

$$11.716\text{g}HNO_3 \times \frac{1\text{mol}HNO_3}{63.018\text{g}HNO_3} \times \frac{1\text{molCu}}{4\text{mol}HNO_3} \times \frac{63.55\text{gCu}}{1\text{molCu}} = 2.954\text{gCu} \tag{1.1.6.15}$$

The remaining mass of Cu is therefore 4.523 g – 2.954 g = **1.569 g**.

b) As we found in part a, we will form **4.277 g of NO_2**.

c) Calculate the mass of $Cu(NO_3)_2$ that should be formed (the theoretical yield):

$$11.716\text{g}HNO_3 \times \frac{1\text{mol}HNO_3}{63.018\text{g}HNO_3} \times \frac{1\text{molCu}\,(NO_3)_2}{4\text{mol}HNO_3} \times \frac{187.57\text{gCu}\,(NO_3)_2}{1\text{molCu}\,(NO_3)_2} = 8.718\text{gCu}\,(NO_3)_2 \tag{1.1.6.16}$$

The percent yield is: $\frac{8.333g}{8.718g} \times 100\% = 95.58\%$

Example 1.1.6.3: Working with Ice Tables

Stoichiometry problems can be approached by using "ICE" tables to organize your thoughts. ICE stands for "**I**nitial moles", "**C**hange in moles", and "**E**nd number of moles." Complete the following ICE tables. For each of these tables, the relevant reaction is:

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O \tag{1.1.6.17}$$

Stoichiometry Table

a)	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	2.474 mol	5.131 mol	0 mol	0 mol
Change				
End				

Answer (a)

As in any stoichiometry problem where you are given the numbers of moles of each reactant, you must first determine the limiting reactant. In an ICE table, a simple way to do this (if it isn't immediately obvious) is to assume that the first reactant is completely used up and calculate the number of moles of the other reactant(s) that will be consumed. Then check to be sure that you aren't using more moles than you started with.

For example, let's assume that all of the C_2H_6 is consumed. How much O_2 will we use?

$2.474\text{mol}C_2H_6 \times \frac{7\text{mol}O_2}{2\text{mol}C_2H_6} = 8.659\text{mol}O_2$ will be used

Inserting these numbers into the table gives us:

Stoichiometry Table

	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	2.474 mol	5.131 mol	0 mol	0 mol
Change	– 2.474 mol	– 8.659 mol		
End	0 mol	**-3.528 mol**		

We end up with a negative amount of oxygen, because we used more moles than we were given. This is obviously impossible, so O_2 must be the limiting reactant. Once we know this, it is straightforward to complete the table. The amount of C_2H_6 that we use up is:

$$5.131 \text{mol} O_2 \times \frac{2 \text{mol} C_2H_6}{7 \text{mol} O_2} = 1.466 \text{mol} C_2H_6$$

The amount of CO_2 that we make is:

$$5.131 \text{mol} O_2 \times \frac{4 \text{mol} CO_2}{7 \text{mol} O_2} = 2.932 \text{mol} CO_2$$

The amount of H_2O that we make is calculated similarly. The completed table looks like this:

Stoichiometry Table

	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	2.474 mol	5.131 mol	0 mol	0 mol
Change	**– 1.466 mol**	**– 5.131 mol**	**+ 2.932 mol**	**+ 4.398 mol**
End	**1.008 mol**	**0 mol**	**2.932 mol**	**4.398 mol**

Stoichiometry Table

b)	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	0.0518 mol	0.2331 mol	0.0489 mol	0 mol
Change				
End				

Answer (b)

In this table, we have some CO_2 (a product) in the initial mixture. This does not affect any of our calculations; the CO_2 we make in the reaction just gets added to this initial amount.

In this case, the limiting reactant is C_2H_6. You can determine this using the same method we used in part a. The completed table looks like this:

Stoichiometry Table

	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	0.0518 mol	0.2331 mol	0.0489 mol	0 mol
Change	**– 0.0518 mol**	**–0.1813 mol**	**+ 0.1036 mol**	**+ 0.1554 mol**
End	**0 mol**	**0.0518 mol**	**0.1525 mol**	**0.1554 mol**

Example 1.1.6.4: Stoichiometry and Algebraic Variables

The mole-to-mol ratios in a balanced chemical equation are at the heart of reaction stoichiometry. In fact, you can consider the amounts of reactants mixed together in terms of variable and *still* work through a stoichiometry problem. We will again use "ICE" tables to organize our thoughts. Complete the following ICE tables. For each of these tables, the relevant reaction is:

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O \tag{1.1.6.18}$$

Stoichiometry Table

a)	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	x mol	2x mol	0 mol	0 mol
Change				
End				

Answer (a)

What do we do with variables?? We treat them the same we treat numbers! Let's assume that all of the C_2H_6 is consumed, just as did in part a. How much O_2 will we use?

$$x\,\text{mol}\,C_2H_6 \times \frac{7\text{mol}O_2}{2\text{mol}C_2H_6} = 3.5x\text{mol}O_2 \text{ will be used} \tag{1.1.6.19}$$

If we use x mol of C_2H_6 and 3.5x mol of O_2, our table will look like this:

Stoichiometry Table

	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	x mol	2x mol	0 mol	0 mol
Change	– x mol	– 3.5x mol		
End	0 mol	**-1.5x mol**		

As in part a of Exercise 1.1.6.3, if we use all of the C_2H_6, we use more O_2 than we actually have. Therefore, O_2 must be the limiting reactant. The amount of C_2H_6 we use is:

$$2x\,\text{mol}\,O_2 \times \frac{2\,\text{mol}\,C_2H_6}{7\text{mol}O_2} = \frac{4}{7}x\text{mol}C_2H_6 = 0.5714x\text{mol}C_2H_6 \tag{1.1.6.20}$$

The amount of CO_2 we make is:

$$2x\,\text{mol}\,O_2 \times \frac{4\text{mol}CO_2}{7\text{mol}O_2} = \frac{8}{7}x\text{mol}CO_2 = 1.1429x\text{mol}CO_2 \tag{1.1.6.21}$$

The amount of H_2O we make is:

$$2x\,\text{mol}\,O_2 \times \frac{6\text{mol}H_2O}{7\text{mol}O_2} = \frac{12}{7}x\text{mol}H_2O = 1.7143x\text{mol}H_2O \tag{1.1.6.22}$$

The completed table looks like this:

Stoichiometry Table

	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	x mol	2x mol	0 mol	0 mol
Change	**– 0.5714x mol**	**– 2x mol**	**+ 1.1429x mol**	**+ 1.7143x mol**
End	**0.4286x mol**	**0 mol**	**1.1429x mol**	**1.7143x mol**

(You can also express all of the moles as fractions. The final numbers will be $^{3}/_{7}x$ mol C_2H_6, $^{8}/_{7}x$ mol CO_2, and $^{12}/_{7}x$ mol H_2O.)

For part b, complete the table assuming that C_2H_6 is the limiting reactant.

Stoichiometry Table

b)	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	x mol	y mol	0 mol	0 mol
Change				
End				

Answer (b)

We are told that C_2H_6 is the limiting reactant, so all of the amounts in the "change" row will be based on the initial moles of C_2H_6. The amount of O_2 that we use is:

$$x\,\text{mol}\,C_2H_6 \times \frac{7\text{mol}O_2}{2\text{mol}C_2H_6} = 3.5x\text{mol}O_2 \tag{1.1.6.23}$$

The amount of CO_2 we make will be:

$$x\,\text{mol}\,C_2H_6 \times \frac{4\text{mol}CO_2}{2\text{mol}C_2H_6} = 2x\text{mol}CO_2 \tag{1.1.6.24}$$

The amount of H_2O we make will be:

$$x\,\text{mol}\,C_2H_6 \times \frac{6\text{mol}H_2O}{2\text{mol}C_2H_6} = 3x\text{mol}H_2O \tag{1.1.6.25}$$

The completed table looks like this:

Stoichiometry Table

	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	x mol	y mol	0 mol	0 mol
Change	**$-x$ mol**	**$-3.5x$ mol**	**$+2x$ mol**	**$+3x$ mol**
End	**0 mol**	**$y-3.5x$ mol**	**$2x$ mol**	**$3x$ mol**

For part c, complete the table assuming that O_2 is the limiting reactant.

Stoichiometry Table

c)	2 C_2H_6	7 O_2	4 CO_2	6 H_2O
Initial	x mol	y mol	0 mol	0 mol
Change				
End				

Answer (c)

Now we are told that O_2 is the limiting reactant. You should be able to figure out the amounts in the "change" row using the same method we used in parts b and c. The completed table looks like this:

Stoichiometry Table

	$2\ C_2H_6$	$7\ O_2$	$4\ CO_2$	$6\ H_2O$
Initial	x mol	y mol	0 mol	0 mol
Change	**$-0.2857y$ mol**	**$-y$ mol**	**$+0.5714y$ mol**	**$+0.8571y$ mol**
End	**$x - 0.2857y$ mol**	**0 mol**	**$0.5714y$ mol**	**$0.8571y$ mol**

As in part b, you can also express the amounts as fractions if you choose. The final numbers will be $x - {}^{2}/_{7}y$ mol C_2H_6, ${}^{4}/_{7}y$ mol CO_2, and ${}^{6}/_{7}y$ mol H_2O.

Summary

The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

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:

$$moles\ glucose = 45.3\ g\ glucose \times \frac{1\ mol\ glucose}{180.2\ g\ glucose} = 0.251\ mol\ glucose \tag{1.1.6.26}$$

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

$$moles\ CO_2 = mol\ glucose \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \tag{1.1.6.27}$$

$$= 0.251\ mol\ glucose \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \tag{1.1.6.28}$$

$$= 1.51\ mol\ CO_2 \tag{1.1.6.29}$$

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1.1.7: Limiting Reactants

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

$$\text{1 box mix} + \text{2 eggs} \rightarrow \text{1 batch brownies} \tag{1.1.7.1}$$

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.

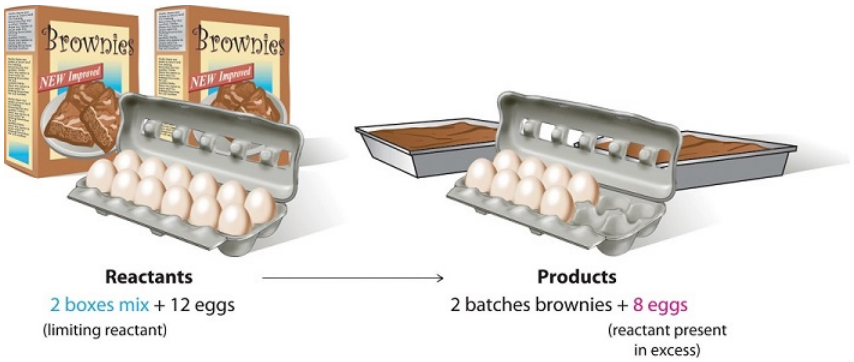


Figure **1.1.7.1**: *The Concept of a Limiting Reactant in the Preparation of Brownies*

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 ($\mathrm{TiCl_4}$) and carbon dioxide.

$$\mathrm{TiO_2\,(s) + 2\ Cl_2\,(g)\ \rightarrow TiCl_4\,(g) + CO_2\,(g)} \tag{1.1.7.2}$$

Titanium tetrachloride is then converted to metallic titanium by reaction with molten magnesium metal at high temperature:

$$\mathrm{TiCl_4\,(g) + 2\ Mg\,(l)\ \rightarrow Ti\,(s) + 2\ MgCl_2\,(l)} \tag{1.1.7.3}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances, magnesium metal is the limiting reactant in the production of metallic titanium.



Figure **1.1.7.2**: *Medical use of titanium. Here is an example of its successful use in joint replacement implants. An A-P X-ray of a pelvis showing a total hip joint replacement. The right hip joint (on the left in the photograph) has been replaced. A metal prostheses is cemented in the top of the right femur and the head of the femur has been replaced by the rounded head of the prosthesis. 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 Equation 1.1.7.3?

Solving this type of problem requires that you carry out the following steps

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

Step 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:

$$\begin{aligned}\text{moles } \mathrm{TiCl_4} &= \frac{\text{mass } \mathrm{TiCl_4}}{\text{molar mass } \mathrm{TiCl_4}} \\ &= 1000 \cancel{g}\ \mathrm{TiCl_4} \times \frac{1\, mol\ TiCl_4}{189.679 \cancel{g}\ \mathrm{TiCl_4}} \\ &= 5.272\, mol\ \mathrm{TiCl_4} \end{aligned} \tag{1.1.7.4}$$

$$\begin{aligned}\text{moles Mg} &= \frac{\text{mass Mg}}{\text{molar mass Mg}} \\ &= 200 \cancel{g}\ \mathrm{Mg} \times \frac{1\, mol\, \mathrm{Mg}}{24.305 \cancel{g}\ \mathrm{Mg}} \\ &= 8.23\, \mathrm{mol\ Mg} \end{aligned} \tag{1.1.7.5}$$

Step 2: There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol\, \mathrm{Mg}}{mol\, \mathrm{TiCl_4}} = \frac{8.23\, mol}{5.272\, mol} = 1.56 \tag{1.1.7.6}$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2\, mol\, \mathrm{Mg}}{1\, mol\, \mathrm{TiCl_4}} = 2 \tag{1.1.7.7}$$

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 $\mathbf{TiCl_4}$ are required for complete reaction. Because there are 5.272 mol of $\mathbf{TiCl_4}$, titanium tetrachloride is present in excess. Conversely, 5.272 mol of $\mathbf{TiCl_4}$ requires 2 × 5.272 = 10.54 mol of Mg, but there are only 8.23 mol. Therefore, magnesium is the limiting reactant.

Step 3: Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$mol\ \text{Ti} = 8.23\,mol\ \text{Mg} = \frac{1\,mol\ \text{Ti}}{2\,mol\ \text{Mg}} = 4.12\,mol\ \text{Ti} \tag{1.1.7.8}$$

Thus only 4.12 mol of Ti can be formed.

Step 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):

$$\begin{aligned}\text{moles Ti} &= \text{mass Ti} \times \text{molar mass Ti} \\ &= 4.12\,mol\ \text{Ti} \times \frac{47.867\,g\ \text{Ti}}{1\,mol\ \text{Ti}} \\ &= 197\,g\ \text{Ti}\end{aligned}$$

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:

$$TiCl_4 : \frac{5.272\,mol\,(actual)}{1\,mol\,(stoich)} = 5.272$$

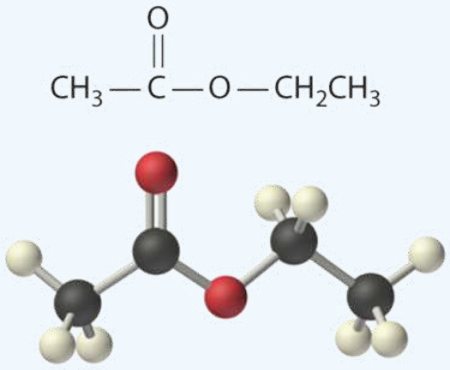
$$Mg : \frac{8.23\,mol\,(actual)}{2\,mol\,(stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

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 **1.1.7.1** demonstrates.

Example 1.1.7.1: Fingernail Polish Remover

Ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol ($\text{C}_2\text{H}_5\text{OH}$) with acetic acid ($\text{CH}_3\text{CO}_2\text{H}$); 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:

$$C_2H_5OH\,(l) + CH_3CO_2H\,(aq) \rightarrow CH_3CO_2C_2H_5\,(aq) + H_2O\,(l)$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall that the density of a substance is the mass divided by the volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

$$\begin{aligned}
\text{moles } C_2H_5OH &= \frac{\text{mass } C_2H_5OH}{\text{molar mass } C_2H_5OH} \\
&= \frac{(\text{volume } C_2H_5OH) \times (\text{density } C_2H_5OH)}{\text{molar mass } C_2H_5OH} \\
&= 10.0 \cancel{ml}\ C_2H_5OH \times \frac{0.7893 \cancel{g}\ C_2H_5OH}{1 \cancel{ml}\ C_2H_5OH} \times \frac{1\,mol\ C_2H_5OH}{46.07 \cancel{g}\ C_2H_5OH} \\
&= 0.171\,mol\ C_2H_5OH \\
\text{moles } CH_3CO_2H &= \frac{\text{mass } CH_3CO_2H}{\text{molar mass } CH_3CO_2H} \\
&= \frac{(\text{volume } CH_3CO_2H) \times (\text{density } CH_3CO_2H)}{\text{molar mass } CH_3CO_2H} \\
&= 10.0 \cancel{ml}\ CH_3CO_2H \times \frac{1.0492 \cancel{g}\ CH_3CO_2H}{1 \cancel{ml}\ CH_3CO_2H} \times \frac{1\,mol\ CH_3CO_2H}{60.05 \cancel{g}\ CH_3CO_2H} \\
&= 0.175\,mol\ CH_3CO_2H
\end{aligned}$$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned}
\textit{moles}\ \text{ethyl acetate} &= \textit{mol}\,\text{ethanol} \times \frac{1\,mol\ \text{ethyl acetate}}{1\,mol\ \text{ethanol}} \\
&= 0.171\,mol\ C_2H_5OH \times \frac{1\,mol\ CH_3CO_2C_2H_5}{1\,mol\ C_2H_5OH} \\
&= 0.171\,mol\ CH_3CO_2C_2H_5
\end{aligned}$$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned}
\text{mass of ethyl acetate} &= \textit{mol}\ \text{ethyl acetate} \times \text{molar mass ethyl acetate} \\
&= 0.171\,mol\,CH_3CO_2C_2H_5 \times \frac{88.11\,g\,CH_3CO_2C_2H_5}{1\,mol\,CH_3CO_2C_2H_5} \\
&= 15.1\,g\,CH_3CO_2C_2H_5
\end{aligned}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm3) to determine the volume of ethyl acetate that could be produced:

$$\text{volume of ethyl acetate} = 15.1\,g\,CH_3CO_2C_2H_5 \times \frac{1\,ml\,CH_3CO_2C_2H_5}{0.9003\,g\,CH_3CO_2C_2H_5}$$

$$= 16.8\,ml\,CH_3CO_2C_2H_5$$

Exercise 1.1.7.1

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 1.1.7.2.

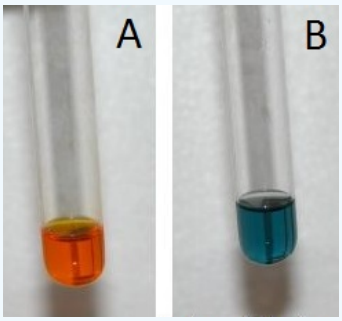
Example 1.1.7.2: Breathalyzer reaction

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:

$$3\,CH_3\,CH_2\,OH\,(aq) + 2\underset{yellow-orange}{Cr_2\,O_7^{2-}}(aq)$$

$$+ 16\,H^+\,(aq) \xrightarrow[H_2SO_4\,(aq)]{Ag^+} 3\,CH_3CO_2H\,(aq) + 4\underset{green}{Cr^{3+}}(aq) + 11\,H_2O\,(l)$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $Cr_2O_7^{2-}$ ions are reduced from Cr^{6+} to Cr^{3+}. In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $Cr_2O_7^{2-}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.



A Breathalyzer 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.

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:

$$\text{percent yield} = \frac{\text{actual yield } (g)}{\text{theoretical yield } (g)} \times 100\% \tag{1.1.7.9}$$

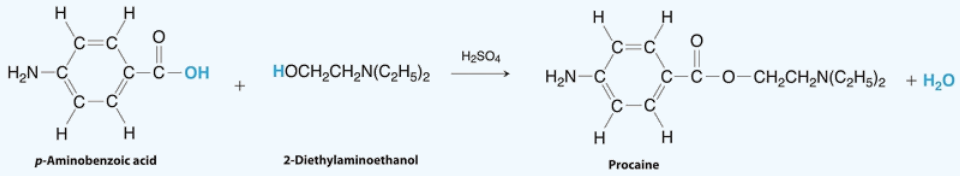
The method used to calculate the percent yield of a reaction is illustrated in Example **1.1.7.4**.

Example 1.1.7.4: 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

$$\underset{\text{p-amino benzoic acid}}{C_7H_7NO_2} + \underset{\text{2-diethylaminoethanol}}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{\text{procaine}}{C_{13}H_{20}N_2O_2} + H_2O$$

If this reaction were carried out with 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:

$$mol \text{ p-aminobenzoic acid} = 10.0\,g \times \frac{1\,mol}{137.14\,g} = 0.0729\,mol \text{ p-aminbenzoic acid}$$

$$mol \text{ 2-diethylaminoethanol} = 10.0\,g \times \frac{1\,mol}{117.19\,g} = 0.0853\,mol \text{ 2-diethylaminoethanol}$$

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.

$$\text{theoretical yield of procaine} = 0.0729\,mol \times \frac{236.31\,g}{1\,mol} = 17.2\,g$$

C The actual yield was only 15.7 g of procaine, so the percent yield (via Equation 1.1.7.9) is

$$\text{percent yield} = \frac{15.7\,g}{17.2\,g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

Exercise 1.1.7.4: 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:

$$2\,PbS\,(s) + 3\,O_2 \rightarrow 2\,PbO\,(s) + 2\,SO_2\,(g)$$

The resulting **PbO** is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$PbO\,(s) + C\,(s) \rightarrow Pb\,(l) + CO\,(g)$$

If 93.3 kg of **PbO** is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?



Electrolytically refined pure (99.989 %) superficially oxidized lead nodules and a high purity (99.989 %) $1\ cm^3$ *lead cube for comparison.* 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.

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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SECTION OVERVIEW

Topic B- Reactions in Aqueous Solution

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

1. Predict and write net ionic equations for the following reaction types:
   a. Acid-base reactions involving OH^- reacting with a strong or a weak acid.
   b. Acid-base reactions involving NH_3 reacting with a strong or a weak acid.
   c. Formation of a weak acid from H^+ and an anion.
   d. Precipitation reactions.
   e. Reactions of carbonates and bicarbonates with acids to form CO_2.
2. Identify an ionic compound as soluble or insoluble in water, based on the solubility rules.
3. Determine any one of the molarity of a solution, the mass of solute, and the volume of solution, given the other two.
4. Solve dilution problems.
5. Solve problems involving aqueous titration.

2.1: Reactions in Aqueous Solution

2.1.1: General Properties of Aqueous Solutions

2.1.1.1: Units of Concentration

2.1.2: Precipitation and Solubility Rules

2.1.3: Acid-Base Reactions

2.1.4: Other Common Reactions

2.1.5: Writing Net Ionic Equations

2.1.6: Concentration of Solutions

2.1.7: Solution Stoichiometry and Chemical Analysis

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CHAPTER OVERVIEW

2.1: Reactions in Aqueous Solution

A solution is a homogeneous mixture in which substances present in lesser amounts, called solutes, are dispersed uniformly throughout the substance in the greater amount, the solvent. An aqueous solution is a solution in which the solvent is water, whereas in a nonaqueous solution, the solvent is a substance other than water. Familiar examples of nonaqueous solvents are ethyl acetate, used in nail polish removers, and turpentine, used to clean paint brushes. In this chapter, we focus on reactions that occur in aqueous solution.

There are many reasons for carrying out reactions in solution. For a chemical reaction to occur, individual atoms, molecules, or ions must collide, and collisions between two solids, which are not dispersed at the atomic, molecular, or ionic level, do not occur at a significant rate. In addition, when the amount of a substance required for a reaction is so small that it cannot be weighed accurately, using a solution of that substance, in which the solute is dispersed in a much larger mass of solvent, enables chemists to measure its quantity with great precision. Chemists can also more effectively control the amount of heat consumed or produced in a reaction when the reaction occurs in solution, and sometimes the nature of the reaction itself can be controlled by the choice of solvent.

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.

2.1.1: General Properties of Aqueous Solutions

2.1.1.1: Units of Concentration

2.1.2: Precipitation and Solubility Rules

2.1.3: Acid-Base Reactions

2.1.4: Other Common Reactions

2.1.5: Writing Net Ionic Equations

2.1.6: Concentration of Solutions

2.1.7: Solution Stoichiometry and Chemical Analysis

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2.1.1: General Properties 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 **2.1.1.1**, 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 **2.1.1.1**). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

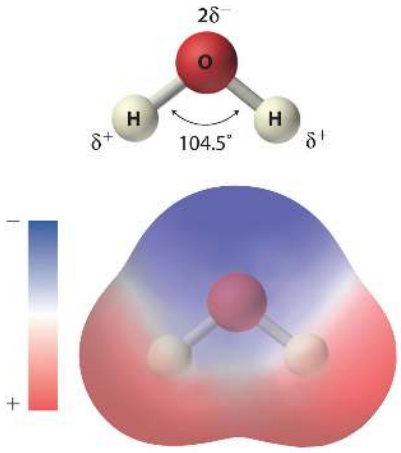


Figure 2.1.1.1: The Polar Nature of Water. *Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) 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 **2.1.1.2**). 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!

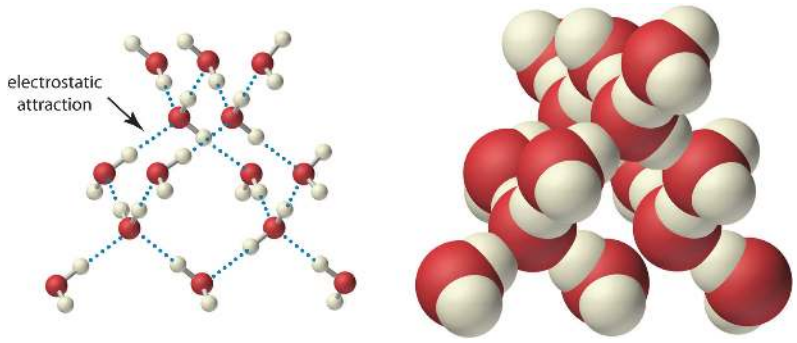


***Figure* 2.1.1.2**: *The Structure of Liquid Water. Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule 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 **2.1.1.3**). 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

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq) \tag{2.1.1.1}$$

where (aq) indicates that Na^+ and Cl^- are hydrated ions.

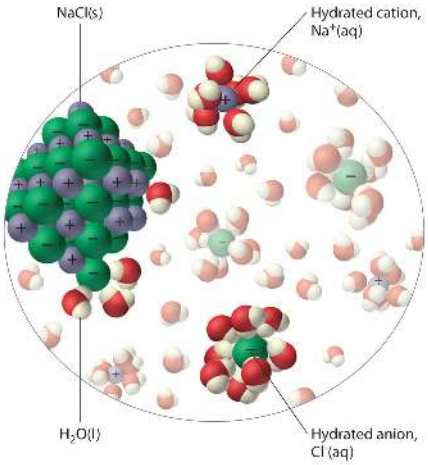


Figure 2.1.1.3: The Dissolution of Sodium Chloride in Water. *An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.*

> *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 **2.1.1.4**). 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 **2.1.1.4** 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.

> *Solutions that contain ions conduct electricity.*

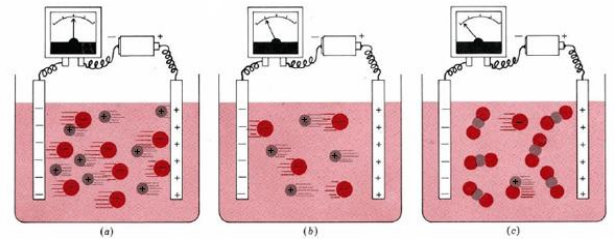


Figure* 2.1.1.4*: *The conductivity of electrolyte solutions: (a) 0.1 M NaCl; (b) 0.05 M NaCl; (c) 0.1 M $HgCl_2$. An electrolyte solution conducts electricity because of the movement of ions in the solution. The larger the concentration of ions, the better the solution conducts. Weak electrolytes, such as $HgCl_2$, conduct badly because they produce very few ions when dissolved and exist mainly in the form of molecules. Figure used with permission from ChemePrime.*

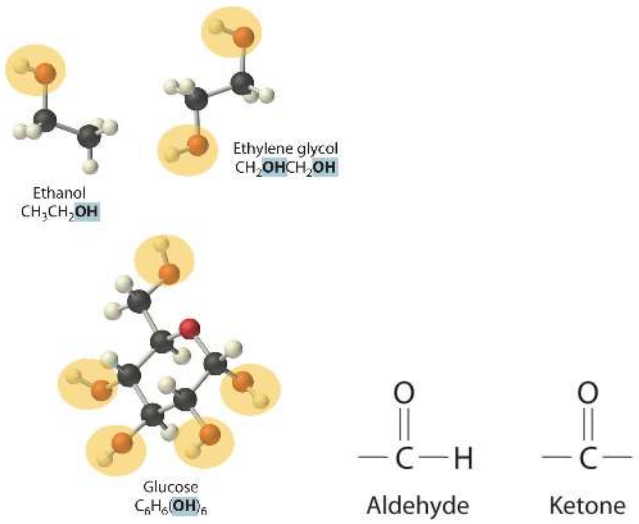
An electrolyte is any compound that can form ions when dissolved in water. Electrolytes may be strong or weak. When strong electrolytes dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure **2.1.1.4**). Examples include ionic compounds such as barium chloride ($BaCl_2$) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

$$BaCl_2(s) \xrightarrow{H_2O(l)} Ba^{2+}(aq) + 2Cl^-(aq) \tag{2.1.1.2}$$

$$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq) \tag{2.1.1.3}$$

The single arrows from reactant to products in Equations 2.1.1.2 and 2.1.1.3 indicate that dissociation is **complete**.

When weak electrolytes dissolve, they produce relatively few ions in solution. This does *not* necessarily 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 later.



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 **2.1.1.5**.

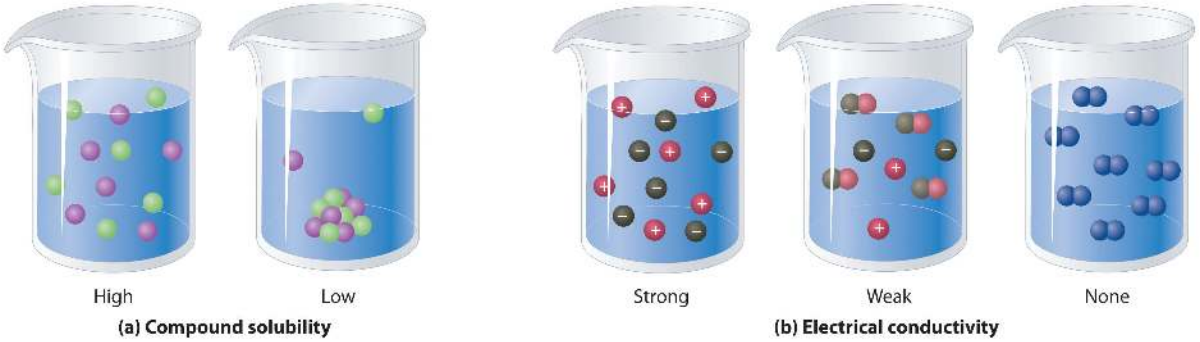


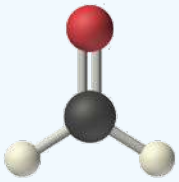
Figure 2.1.1.5: The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b). *When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated 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.*

> *Ionic substances and carboxylic acids are electrolytes; alcohols, aldehydes, and ketones are nonelectrolytes.*

Example 2.1.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. formaldehyde



Formaldehyde, CH_2O

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.

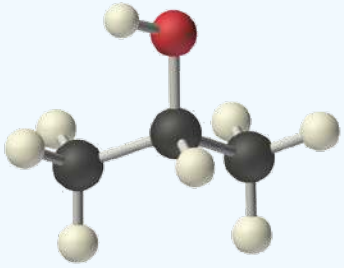
Solution:

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 2.1.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. $(CH_3)_2CHOH$ (2-propanol)



2-Propanol (isopropyl alcohol), $(CH_3)_2CHOH$

b. ammonium sulfate

Answer

a. nonelectrolyte
b. strong electrolyte

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.

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2.1.1.1: Units of Concentration

Solutions are *homogeneous mixtures* containing one or more **solutes** in a **solvent**. The solvent that makes up most of the solution, whereas a solute is the substance that is dissolved inside the solvent.

Relative Concentration Units

Concentrations are often expressed in terms of relative unites (e.g. percentages) with three different types of percentage concentrations commonly used:

1. **Mass Percent**: The mass percent is used to express the concentration of a solution when the mass of a solute and the mass of a solution is given:

$$\text{Mass Percent} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100\% \tag{2.1.1.1.1}$$

2. **Volume Percent**: The volume percent is used to express the concentration of a solution when the volume of a solute and the volume of a solution is given:

$$\text{Volume Percent} = \frac{\text{Volume of Solute}}{\text{Volume of Solution}} \times 100\% \tag{2.1.1.1.2}$$

3. **Mass/Volume Percent:** Another version of a percentage concentration is mass/volume percent, which measures the mass or weight of solute in grams (e.g., in grams) vs. the volume of solution (e.g., in mL). An example would be a 0.9%(w/v) $NaCl$ solution in medical saline solutions that contains 0.9 g of $NaCl$ for every 100 mL of solution (see figure below). The mass/volume percent is used to express the concentration of a solution when the mass of the solute and volume of the solution is given. Since the numerator and denominator have different units, this concentration unit is not a true relative unit (e.g. percentage), however it is often used as an easy concentration unit since volumes of solvent and solutions are easier to measure than weights. Moreover, since the density of dilute aqueous solutions are close to 1 g/mL, if the volume of a solution in measured in mL (as per definition), then this well approximates the mass of the solution in grams (making a true reletive unit (m/m)).

$$\text{Mass/Volume Percent} = \frac{\text{Mass of Solute (g)}}{\text{Volume of Solution (mL)}} \times 100\% \tag{2.1.1.1.3}$$



Figure used with permission from Wikipedia.

Example 2.1.1.1.1: Alcohol "Proof" as a Unit of Concentration

For example, In the United States, alcohol content in spirits is defined as twice the percentage of alcohol by volume (v/v) called proof. What is the concentration of alcohol in *Bacardi 151* spirits that is sold at 151 proof (hence the name)?



Figure: A mostly-empty bottle of Bacardi 151. from Wikipedia.

Solution

It will have an alcohol content of 75.5% (w/w) as per definition of "proof".

When calculating these percentages, that the units of the solute and solution should be equivalent units (and weight/volume percent (w/v %) is defined in terms of grams and mililiters).

You CANNOT plug in…	You CANNOT plug in…
(2 g Solute) / (1 kg Solution)	(2 g Solute) / (1000 g Solution)
	or (0.002 kg Solute) / (1 kg Solution)
(5 mL Solute) / (1 L Solution)	(5 mL Solute) / (1000 mL Solution)
	or (0.005 L Solute) / (1 L Solution)
(8 g Solute) / (1 L Solution)	(8 g Solute) / (1000 mL Solution)
	or (0.008 kg Solute) / (1 L Solution)

Dilute Concentrations Units

Sometimes when solutions are too dilute, their percentage concentrations are too low. So, instead of using really low percentage concentrations such as 0.00001% or 0.000000001%, we choose another way to express the concentrations. This next way of expressing concentrations is similar to cooking recipes. For example, a recipe may tell you to use 1 part sugar, 10 parts water. As you know, this allows you to use amounts such as 1 cup sugar + 10 cups water in your equation. However, instead of using the recipe's "1 part per ten" amount, chemists often use *parts per million*, *parts per billion* or *parts per trillion* to describe dilute concentrations.

- **Parts per Million**: A concentration of a solution that contained 1 g solute and 1000000 mL solution (same as 1 mg solute and 1 L solution) would create a very small percentage concentration. Because a solution like this would be so dilute, the density of the solution is well approximated by the density of the solvent; for water that is 1 g/mL (but would be different for different solvents). So, after doing the math and converting the milliliters of solution into grams of solution (assuming water is the solvent):

$$\frac{1\text{ g solute}}{1000000\text{ mL solution}} \times \frac{1\text{ mL}}{1\text{ g}} = \frac{1\text{ g solute}}{1000000\text{ g solution}} \tag{2.1.1.1.4}$$

  We get (1 g solute)/(1000000 g solution). Because both the solute and the solution are both now expressed in terms of grams, it could now be said that the solute concentration is 1 part per million (ppm).

$$1\text{ ppm} = \frac{1\text{ mg Solute}}{1\text{ L Solution}} \tag{2.1.1.1.5}$$

  The ppm unit can also be used in terms of volume/volume (v/v) instead (see example below).

- **Parts per Billion**: Parts per billion (ppb) is almost like ppm, except 1 ppb is 1000-fold more dilute than 1 ppm.

$$1 \text{ ppb} = \frac{1 \ \mu\text{g Solute}}{1 \text{ L Solution}} \tag{2.1.1.1.6}$$

- **Parts per Trillion**: Just like ppb, the idea behind parts per trillion (ppt) is similar to that of ppm. However, 1 ppt is 1000-fold more dilute than 1 ppb and 1000000-fold more dilute than 1 ppm.

$$1 \text{ ppt} = \frac{1 \text{ ng Solute}}{1 \text{ L Solution}} \tag{2.1.1.1.7}$$

Example 2.1.1.1.2: ppm in the Atmosphere

Here is a table with the volume percent of different gases found in air. Volume percent means that for 100 L of air, there are 78.084 L Nitrogen, 20.946 L Oxygen, 0.934 L Argon and so on; Volume percent mass is different from the composition by mass or composition by amount of moles.

Elements Name	Volume Percent (v/v)	ppm (v/v)
Nitrogen	78.084	780,840
Oxygen	20.946	209,460
Water Vapor	4.0%	40,000
Argon	0.934	9,340
Carbon Dioxide	0.0379	379* (but growing rapidly)
Neon	0.008	8.0
Helium	0.000524	5.24
Methane	0.00017	1.7
Krypton	0.000114	1.14
Ozone	0.000001	0.1
Dinitrogen Monoxide	0.00003	0.305

Concentration Units based on moles

- **Mole Fraction**: The mole fraction of a substance is the fraction of all of its molecules (or atoms) out of the total number of molecules (or atoms). It can also come in handy sometimes when dealing with the $PV = nRT$ equation.

$$\chi_A = \frac{\text{number of moles of substance A}}{\text{total number of moles in solution}} \tag{2.1.1.1.8}$$

  Also, keep in mind that the sum of each of the solution's substances' mole fractions equals 1.

$$\chi_A + \chi_B + \chi_C + \ldots = 1 \tag{2.1.1.1.9}$$

- **Mole Percent**: The mole percent (of substance A) is χ_A in percent form.

$$\text{Mole percent (of substance A)} = \chi_A \times 100\% \tag{2.1.1.1.10}$$

- **Molarity**: The molarity (M) of a solution is used to represent the amount of moles of solute per liter of the solution.

$$M = \frac{\text{Moles of Solute}}{\text{Liters of Solution}} \tag{2.1.1.1.11}$$

- **Molality**: The molality (m) of a solution is used to represent the amount of moles of solute per kilogram of the solvent.

$$m = \frac{\text{Moles of Solute}}{\text{Kilograms of Solvent}} \tag{2.1.1.1.12}$$

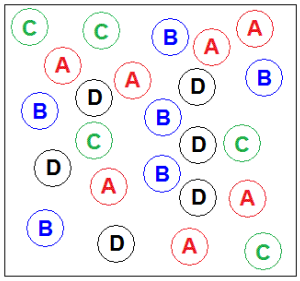


Figure: Different molarities of liquids in the laboratory. 50 ml of distilled water (0 M), Sodium Hydroxide solution of 0.1 M, and Hydrochloric acid solution of 0.1 M. from group4swimmingpool.

The molarity and molality equations differ only from their denominators. However, this is a huge difference. As you may remember, volume varies with different temperatures. At higher temperatures, volumes of liquids increase, while at lower temperatures, volumes of liquids decrease. Therefore, molarities of solutions also vary at different temperatures. This creates an advantage for using molality over molarity. Using molalities rather than molarities for lab experiments would best keep the results within a closer range. Because volume is not a part of its equation, it makes molality independent of temperature.

Practice Problems

1. In a solution, there is 111.0 mL (110.605 g) solvent and 5.24 mL (6.0508 g) solute present in a solution. Find the mass percent, volume percent and mass/volume percent of the solute.
2. With the solution shown in the picture below, find the mole percent of substance C.



Molecule	Amount Present in Box
A	7
B	6
C	5
D	6
total	24

3. A 1.5L solution is composed of 0.25g NaCl dissolved in water. Find its molarity.
4. 0.88g NaCl is dissolved in 2.0L water. Find its molality.

Solutions

1:

Mass Percent

$$=(\text{Mass of Solute}) / (\text{Mass of Solution}) \times 100\%|$$

$$=(6.0508\text{g}) / (110.605\text{g} + 6.0508\text{g}) \times 100\%$$

$$=(0.0518688312) \times 100\%$$

$$=5.186883121\%$$

Mass Percent= 5.186%

Volume Percent

$$=(\text{Volume of Solute}) / (\text{Volume of Solution}) \times 100\%$$

$$=(5.24\text{mL}) / (111.0\text{mL} + 5.24\text{mL}) \times 100\%$$

$$=(0.0450791466) \times 100\%$$

=4.507914659%

Volume Percent= 4.51%

Mass/Volume Percent

=(Mass of Solute) / (Volume of Solution) x 100%

=(6.0508g) / (111.0mL + 5.24mL) x 100%

=(0.0520) x 100%

=5.205%

Mass/Volume Percent= 5.2054%

2. Moles of C= (5 C molecules) x (1mol C / 6.022×10^{23} C molecules) = $8.30288941 \times 10^{-24}$mol C

Total Moles= (24 molecules) x (1mol / 6.022×10^{23} molecules)= $3.98538691 \times 10^{-23}$mol total

X_C= ($8.30288941 \times 10^{-24}$mol C) / ($3.98538691 \times 10^{-23}$mol) = .2083333333

Mole Percent of C

= X_C x 100%

=(o.2083333333) x 100%

=20.83333333

Mole Percent of C = 20%

3. Moles of NaCl= (0.25g) / (22.99g + 35.45g) = 0.004277 mol NaCl

Molarity

=(Moles of Solute) / (Liters of Solution)

=(0.004277mol NaCl) / (1.5L)

=0.002851 M

Molarity= 0.0029M

4. Moles of NaCl= (0.88g) / (22.99g + 35.45g) = 0.01506 mol NaCl

Mass of water= (2.0L) x (1000mL / 1L) x (1g / 1mL) x (1kg / 1000g) = 2.0kg water

Molality

=(Moles of Solute) / (kg of Solvent)

=(0.01506 mol NaCl) / (2.0kg)

=0.0075290897m

Molality= 0.0075m

References

1. Petrucci, Harwood, Herring. General Chemistry: Principles & Modern Applications. 8th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2002. 528-531

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2.1.2: Precipitation and Solubility Rules

Learning Objectives

- Predict the solubility of common inorganic compounds by using solubility rules
- Write simple net ionic equations for precipitation reactions.

Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in the text chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table **2.1.2.1**).

All compounds that contain the cations Na^+, K^+ or NH_4^+, or the anions NO_3^- or $C_2H_3O_2^-$ are soluble in water. It is best to memorize these. Beyond this, solubilities are normally classified using the anion in the compound. Here are the rules that you will use in Chem 101A:

Table **2.1.2.1**: Solubility Rules for Common Ionic Compounds in Water

An anion from this column...	...combined with a cation from this column produces a **soluble** compound (a precipitate will NOT form)	... combined with a cation from this column produces an **insoluble** compound (a precipitate will form)
NO_3^-, $C_2H_3O_2^-$	All	None
Cl^-, Br^-, I^-	Most	Ag^+ Pb^{2+} Hg_2^{2+}
SO_4^{2-}	Most	Ag^+ Pb^{2+} Hg_2^{2+} Ca^{2+} Sr^{2+} Ba^{2+} (the heavier IIA elements)
OH^-	Na^+ K^+ (NH_4^+ reacts with OH^-: see below) Ba^{2+}	All others (note: Ag^+ forms an oxide product, rather than hydroxide product)
CO_3^{2-}, PO_4^{3-}	Na^+ K^+ NH_4^+	All others
S^{2-}	Na^+ K^+ NH_4^+ Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+} (group IIA)	All others (the reactions of sulfide with 3+ ions are not simple precipitations: you do not need to know these)

Note that the reaction of Ag^+ with OH^- produces Ag_2O (and water), not AgOH. This is a “quirk” of the chemistry of silver ions. The net ionic equation for this reaction is:

$$2\,Ag^+(aq) + 2\,OH^-(aq) \rightarrow Ag_2O(s) + H_2O(l) \qquad (2.1.2.1)$$

Note that ammonia (NH_3) dissolves in water to produce a small concentration of hydroxide ions (discussed in a later section.) The resulting hydroxide ions can participate in precipitation reactions. Here is an example, using Mg^{2+}:

$$\mathrm{Mg^{2+}(aq) + 2\,NH_3(aq) + 2\,H_2O(l) \rightarrow Mg(OH)_2(s) + 2\,NH_4{}^+(aq)} \tag{2.1.2.2}$$

Note that the above equation is written in terms of the major species in solution (NH_3 and H_2O) as opposed to the minor species (NH_4+ and OH-).

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide. This observation is consistent with the solubility guidelines given above: The only insoluble combination among all those possible is lead and iodide. The net ionic equation representing this reaction is:

$$\mathrm{Pb^{2+}(aq) + 2\,I^-(aq) \rightarrow PbI_2(s)} \tag{2.1.2.3}$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure **2.1.2.1**). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.



Figure **2.1.2.1**: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table **2.1.2.1** may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium chloride will yield a solution containing Ag^+, $NO_3{}^-$, Na^+, and Cl^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaCl, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgCl. The solubility guidelines indicate all nitrate salts are soluble but that AgCl is an insoluble combination. A precipitation reaction, therefore, is predicted to occur, as described by the following equation:

$$\mathrm{Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)} \quad \text{(net ionic)} \tag{2.1.2.4}$$

Example 2.1.2.1: Predicting Precipitation Products

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ba^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s) \quad (2.1.2.5)$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \quad (2.1.2.6)$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$Pb^{2+}(aq) + CO_3{}^{2-}(aq) \rightarrow PbCO_3(s) \quad (2.1.2.7)$$

Exercise 2.1.2.1

Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Answer

sodium sulfate, $BaSO_4$

Glossary

insoluble

of relatively low solubility; dissolving only to a slight extent

precipitate

insoluble product that forms from reaction of soluble reactants

precipitation reaction

reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

salt

ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

soluble

of relatively high solubility; dissolving to a relatively large extent

solubility

the extent to which a substance may be dissolved in water, or any solvent

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2.1.3: Acid-Base Reactions

Acid-Base Reactions

An acid-base reaction is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an acid is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

$$\mathbf{HCl}(aq) + \mathbf{H_2O}(aq) \rightarrow \mathbf{Cl^-}(aq) + \mathbf{H_3O^+}(aq) \tag{2.1.3.1}$$

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (Figure **2.1.3.2**).

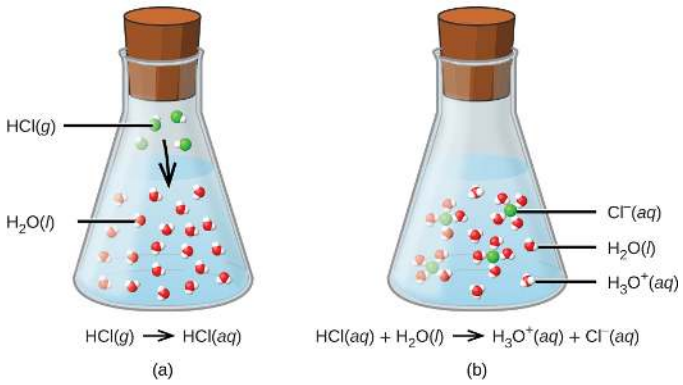
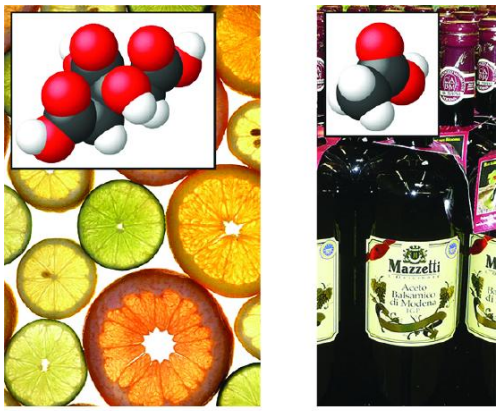


Figure **2.1.3.2**: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions)

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called strong acids, and HCl is one among just a handful of common acid compounds that are classified as strong (Table **2.1.3.1**). A far greater number of compounds behave as weak acids and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{CH_3CO_2^-}(aq) + \mathbf{H_3O^+}(aq) \tag{2.1.3.2}$$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $\mathbf{CH_3CO_2^-}$ (Figure **2.1.3.3**). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)



(a) (b)

Figure **2.1.3.3**: (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

Table **2.1.3.2**: Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

A base is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered strong bases.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

$$\mathrm{NaOH}(s) \rightarrow \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq) \tag{2.1.3.3}$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as weak bases. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure **2.1.3.4**). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{2.1.3.4}$$

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as $\mathrm{NH_4^+}$ ions.



Figure 2.1.3.4: Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions, respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. A neutralization reaction is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a salt and water, and neither reactant is the water itself:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water} \tag{2.1.3.5}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$Mg(OH)_2(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + 2\,H_2O(l). \tag{2.1.3.6}$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example 2.1.3.2: Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

a. the weak acid hydrogen hypochlorite reacts with water
b. a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)n$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO_3^-).

$$Ba(OH)_2(aq) + 2\,HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2\,H_2O(l)n$$

Exercise 2.1.3.21

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)n$$

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2.1.4: Other Common Reactions

Learning Objectives

- Predict the formation of a weak electrolyte from its constituent ions.
- Write the net ionic equation for the formation of a weak electrolyte.
- Predict the formation of carbon dioxide gas from the reaction of carbonate or bicarbonate ions with acid.

Constituent Ions will Associate to form Weak Electrolytes

Recall that weak electrolytes are solutes where only a small percentage of the molecules present dissociate into ions when dissolved in water. We call this partial dissociation. Alternatively, because most of the ions remain associated, we could describe the solution of a weak electrolyte as *mostly molecular*. Either way we describe it, the behavior is consistent. The constituent ions of a weak electrolyte tend are strongly attracted to one another. Therefore, if you mix solutions containing the constituent ions of a weak electrolyte, the ions will associate (the opposite of dissociate) and the major product will be the weak electrolyte.

For example, weak acids--weak electrolytes, by definition--will be formed whenever their constituent ions are mixed. Here are two examples:

Mixing solutions of HCl and $KC_2H_3O_2$, the major product will be acetic acid, $HC_2H_3O_2$.

$$H^+(aq) + C_2H_3O_2{}^-(aq) \rightarrow HC_2H_3O_2(aq) \tag{2.1.4.1}$$

Mixing solutions of HNO_3 and NaF, the major product will be hydrofluoric acid, HF.

$$H^+(aq) + F^-(aq) \rightarrow HF(aq) \tag{2.1.4.2}$$

You have been given one example of a weak base, ammonia. Recognize that combining the ions ammonium ($NH_4{}^+$) and hydroxide (OH^-) will result in the formation of the weak electrolyte, ammonia (NH_3). Here is an example:

Mixing solutions of NaNH4 and KOH, the major product will be ammonia, NH_3.

$$NH_4{}^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l) \tag{2.1.4.3}$$

Special Reactions of Carbonate and Bicarbonate Ions

Carbonate ion and bicarbonate ion react with excess H^+ to form H_2CO_3 (carbonic acid, a weak electrolye). However, carbonic acid can only exist at very low concentrations. Under normal circumstances, carbonic acid decomposes into CO_2 and H_2O. Therefore, carbon dioxide and water are the normal products whenever carbonate or bicarbonate react with excess acid. Here are some examples:

Mixing solutions of $NaHCO_3$ and HCl:

step 1:

$$HCO_3{}^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \tag{2.1.4.4}$$

step 2:

$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) \tag{2.1.4.5}$$

Or, overall:

$$HCO_3{}^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g) \tag{2.1.4.6}$$

Adding a solution of HCl to solid $CaCO_3$ (with the acid in excess):

step 1:

$$CaCO_3(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + HCO_3{}^-(aq) \tag{2.1.4.7}$$

step 2:

$$\mathrm{HCO_3^-}(aq) + \mathrm{H^+}(aq) \rightarrow \mathrm{H_2CO_3}(aq) \tag{2.1.4.8}$$

step 3:

$$\mathrm{H_2CO_3}(aq) \rightarrow \mathrm{H_2O}(l) + \mathrm{CO_2}(g) \tag{2.1.4.9}$$

Overall:

$$\mathrm{CaCO_3}(s) + 2\,\mathrm{H^+}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}(g) \tag{2.1.4.10}$$

Mixing solutions of $HC_2H_3O_2$ and K_2CO_3 (with the acid in excess):

step 1:

$$\mathrm{CO_3^{2-}}(aq) + \mathrm{HC_2H_3O_2}(aq) \rightarrow \mathrm{C_2H_3O_2^-}(aq) + \mathrm{HCO_3^-}(aq) \tag{2.1.4.11}$$

step 2:

$$\mathrm{HCO_3^-}(aq) + \mathrm{HC_2H_3O_2}(aq) + \rightarrow \mathrm{C_2H_3O_2^-}(aq) + \mathrm{H_2CO_3}(aq) \tag{2.1.4.12}$$

step 3:

$$\mathrm{H_2CO_3}(aq) \rightarrow \mathrm{H_2O}(l) + \mathrm{CO_2}(g) \tag{2.1.4.13}$$

Overall:

$$\mathrm{CO_3^{2-}}(aq) + 2\,\mathrm{HC_2H_3O_2}(aq) \rightarrow 2\,\mathrm{C_2H_3O_2^-}(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}(g) \tag{2.1.4.14}$$

You can see an example of this kind of reaction for yourself by mixing baking soda ($NaHCO_3$) and vinegar (a solution of acetic acid) in your kitchen. The mixture will bubble vigorously as gaseous carbon dioxide forms.

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2.1.5: Writing Net Ionic Equations

Learning Objectives

- Identify what species are really present in an aqueous solution.
- Identify possible products: insoluble ionic compound, water, weak electrolyte
- Write net ionic equations for reactions that occur in aqueous solution.

WRITING NET IONIC EQUATIONS FOR CHEM 101A

Chemical reactions that occur in solution are most concisely described by writing net ionic equations. A net ionic equation is the most accurate representation of the actual chemical process that occurs. Writing these equations requires a familiarity with solubility rules, acid-base reactivity, weak electrolytes and special reactions of carbonates and bicarbonates. The following is the strategy we suggest following for writing net ionic equations in Chem 101A.

Step 1: Identify the species that are actually present, accounting for the dissociation of any strong electrolytes. (Insoluble ionic compounds do not ionize, but you must consider the possibility that the ions in an insoluble compound might still be involved in the reaction.)

Step 2: Identify the products that will be formed when the reactants are combined. The most common products are insoluble ionic compounds and water. See the "reactivity of inorganic compounds" handout for more information.

Step 3: Write the balanced equation for the reaction you identified in step 2, being certain to show the major species in your equation. This is the net ionic equation for the reaction.

Example 2.1.5.1: Writing Net Ionic Equations

Write a net ionic equation to describe the reaction that occurs when 0.100 M K_3PO_4 solution is mixed with 0.100 M $Ca(NO_3)_2$ solution

Step 1: The species that are present are:

From the K_3PO_4	From the $Ca(NO_3)_2$
K^+	Ca^{2+}
PO_4^{3-}	NO_3^-

Step 2: There are two possible combinations of ions here: $K^+ + NO_3^-$ (forming KNO_3) and $Ca^{2+} + PO_4^{3-}$ (forming $Ca_3(PO_4)_2$). We know from the general solubility rules that $Ca_3(PO_4)_2$ is an insoluble compound, so it will be formed. KNO_3 is water-soluble, so it will not form.

Step 3: The reaction is the combination of calcium and phosphate ions to form calcium phosphate. The balanced equation for this reaction is:

$$3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s) \qquad (2.1.5.1)$$

Example 2.1.5.2: Writing Net Ionic Equations

Write a net ionic equation to describe the reaction that occurs when 0.1 M $HC_2H_3O_2$ solution is mixed with 0.1 M KOH solution

Step 1: The species that are present are:

From the $HC_2H_3O_2$	From the KOH
H^+	K^+
$C_2H_3O_2^-$	OH^-

Acetic acid, $HC_2H_3O_2$, is a weak acid. Think of the acid molecules as "potential" H^+ and $C_2H_3O_2^-$ ions, however, these "potential" ions are held together by a covalent bond. A small percentage of the acid molecules do actually ionize (break apart into ions) when they dissolve in water, but most of the weak acid molecules do not ionize.

Step 2: Reaction of an acid (source of H^+) and a base (source of OH^-) will form water. The H^+ from the $HC_2H_3O_2$ can combine with the OH^- to form H_2O. Note that $KC_2H_3O_2$ is a water-soluble compound, so it will not form.

Step 3: In order to form water as a product, the covalent bond between the H^+ and the $C_2H_3O_2^-$ ions must break. The H^+ and OH^- will form water. The acetate ion is released when the covalent bond breaks. **Remember to show the major species that exist in solution when you write your equation.** Most of the acid molecules are not ionized, so you must write out the complete formula of the acid in your equation. The balanced equation for this reaction is:

$$\mathbf{HC_2H_3O_2\,(aq) + OH^-\,(aq) \rightarrow H_2O\,(l) + C_2H_3O_2^-\,(aq)} \qquad (2.1.5.2)$$

Example 2.1.5.3: Writing Net Ionic Equations

Write a net ionic equation to describe the reaction that occurs when solid $Mg(OH)_2$ and excess 0.1 M HCl solution

Step 1: The species that are present are:

From the $Mg(OH)_2$ solid	From the HCl
Mg^{2+}	H^+
OH^-	Cl^-

Notice that the magnesium hydroxide is a solid; it is not water soluble. The magnesium ions and the hydroxide ions will remain held together by ionic bonds even if they are in the presence of polar water molecules. However, these individual ions must be considered as possible reactants. Think of the solid ionic compound as a possible source of Mg^{2+} and OH^- ions. If a chemical reaction is possible, the ionic bonds between Mg^{2+} and OH^- will break.

Step 2: Reaction of an acid (source of H^+) and a base (source of OH^-) will form water. The H^+ from the HCl can combine with the OH^- from the solid $Mg(OH)_2$ to form H_2O. Note that $MgCl_2$ is a water-soluble compound, so it will not form.

Step 3: In order to form water as a product, the ionic bond between the magnesium and hydroxide ions must break. The OH^- and H^+ will form water. The magnesium ion is released into solution when the ionic bond breaks. **Remember to show the major species that exist in solution when you write your equation.** The magnesium hydroxide is a solid reactant, so you must write out the complete formula in your equation. The balanced equation for this reaction is:

$$\mathbf{Mg(OH)_2\,(s) + 2\,H^+\,(aq) \rightarrow 2\,H_2O\,(l) + Mg^{2+}\,(aq)} \qquad (2.1.5.3)$$

Example 2.1.5.4: Writing Net Ionic Equations

Write a net ionic equation to describe the reaction that occurs when 0.1 M $KHCO_3$ solution is mixed with excess 0.1 M HNO_3 solution

Step 1: The species that are present are:

From the **$KHCO_3$**	From the **HNO_3**
K^+	H^+
HCO_3^-	NO_3^-

Step 2: From the "reactivity of inorganic compounds" handout, we know that when carbonate or bicarbonate ions react with acids, carbon dioxide and water are the normal products. Be sure to refer to the handout for details of this process.

Step 3: The reaction is the combination of bicarbonate ions and hydrogen ions that will first form carbonic acid (H_2CO_3). However, carbonic acid can only exist at very low concentrations. Under normal circumstances, carbonic acid decomposes into CO_2 and H_2O. The balanced equation for this reaction is:

$$\mathbf{HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)} \qquad (2.1.5.4)$$

Supplemental Exercises: Writing Net Ionic Equations

For each of the following, write the net ionic equation for the reaction that will occur when the two substances are mixed. If no reaction occurs, write "no reaction." *Note: the reactions are grouped according to the difficulty that typical students have with them—our groupings may not match your own experience and ability.* (Answers are available below.)

Easy reactions:

1) 0.1 M $AgNO_3$ and 0.1 M KBr

2) 0.1 M $CaCl_2$ and 0.1 M $NaNO_3$

3) 0.1 M $Fe(NO_3)_3$ and 0.1 M Na_2CO_3

4) 0.1 M KOH and 0.1 M $CoBr_2$

5) 0.1 M HNO_3 and 0.1 M $Ba(OH)_2$

6) 0.1 M $Pb(NO_3)_2$ and 0.1 M $MgSO_4$

7) 0.1 M Na_2S and 0.1 M MnI_2

8) 0.1 M K_3PO_4 and 0.1 M $CuCl_2$

9) 0.1 M HCl and 0.1 M $NaC_2H_3O_2$

10) 0.1 M $NiSO_4$ and 0.1 M $FeCl_3$

Harder reactions:

1) 0.1 M $HC_2H_3O_2$ and 0.1 M KOH

2) 0.1 M NH_3 and 0.1 M HBr

3) 1 M HCl and solid $Mn(OH)_2$

4) excess 1 M HNO_3 and solid $AlPO_4$

5) 0.1 M $AgNO_3$ and 0.1 M NaOH

6) 0.1 M HClO and 0.1 M $Ba(OH)_2$ (no precipitate forms)

Still harder reactions:

1) 0.1 M Na_2HPO_4 and 0.1 M HI (equal volumes)

2) 0.1 M NH_3 and 0.1 M $Fe(NO_3)_2$

3) 0.1 M $NaHCO_3$ and 0.1 M HCl

4) 0.1 M K_2CO_3 and 0.1 M HNO_3 (equal volumes)

5) 0.1 M H_3PO_4 and 0.1 M NH_3 (equal volumes)

Very tricky reactions:

1) 0.1 M $AgNO_3$ and 0.1 M NH_3

2) solid $BaCO_3$ and excess 2 M $HC_2H_3O_2$

3) solid $Cu(OH)_2$ and 1 M H_2SO_4 (equal numbers of moles)

4) solid Ag_2O and excess 2 M HCl

5) 0.1 M H_3PO_4 and excess 1 M KOH

AnswerS TO NET IONIC EQUATIONS PRACTICE PROBLEMS

Easy reactions:

1) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

2) no reaction

3) $2\ Fe^{3+}(aq) + 3\ CO_3^{2-}(aq) \rightarrow Fe_2(CO_3)_3(s)$

4) $2\ OH^-(aq) + Co^{2+}(aq) \rightarrow Co(OH)_2(s)$

5) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

6) $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

7) $S^{2-}(aq) + Mn^{2+}(aq) \rightarrow MnS(s)$

8) $2\ PO_4^{3-}(aq) + 3\ Cu^{2+}(aq) \rightarrow Cu_3(PO_4)_2(s)$

9) $H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq)$

10) no reaction

Harder reactions:

1) $HC_2H_3O_2(aq) + OH^-(aq) \rightarrow C_2H_3O_2^-(aq) + H_2O(l)$

2) $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

3) $2\ H^+(aq) + Mn(OH)_2(s) \rightarrow Mn^{2+}(aq) + 2\ H_2O(l)$

4) $3\ H^+(aq) + AlPO_4(s) \rightarrow Al^{3+}(aq) + H_3PO_4(aq)$

5) $2\ Ag^+(aq) + 2\ OH^-(aq) \rightarrow Ag_2O(s) + H_2O(l)$

6) $HClO(aq) + OH^-(aq) \rightarrow ClO^-(aq) + H_2O(l)$

Still harder reactions:

1) $HPO_4^{2-}(aq) + H^+(aq) \rightarrow H_2PO_4^-(aq)$

2) $Fe^{2+}(aq) + 2\ NH_3(aq) + 2\ H_2O(l) \rightarrow Fe(OH)_2(s) + 2\ NH_4^+(aq)$

3) $HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$

4) $CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$

5) $H_3PO_4(aq) + NH_3(aq) \rightarrow H_2PO_4^-(aq) + NH_4^+(aq)$

Very tricky reactions:

1) $2\ Ag^+(aq) + 2\ NH_3(aq) + H_2O(l) \rightarrow Ag_2O(s) + 2\ NH_4^+(aq)$

2) $BaCO_3(s) + 2\ HC_2H_3O_2(aq) \rightarrow Ba^{2+}(aq) + 2\ C_2H_3O_2^-(aq) + H_2O(l) + CO_2(g)$

3) $Cu(OH)_2(s) + H^+(aq) + HSO_4^-(aq) \rightarrow Cu^{2+}(aq) + 2\ H_2O(l) + SO_4^{2-}(aq)$

4) $Ag_2O(s) + 2\ H^+(aq) + 2\ Cl^-(aq) \rightarrow 2\ AgCl(s) + H_2O(l)$

5) Three reactions will occur, one after the other:

$H_3PO_4(aq) + OH^-(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$

$H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$

$HPO_4^{2-}(aq) + OH^-(aq) \rightarrow PO_4^{3-}(aq) + H_2O(l)$

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2.1.6: Concentration of Solutions

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 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:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{2.1.6.1}$$

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,

$$[\text{sucrose}] = 1.00\ \text{M} \tag{2.1.6.2}$$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{2.1.6.3}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{2.1.6.4}$$

Figure **2.1.6.1** illustrates the use of Equations **2.1.6.3** and **2.1.6.4**.

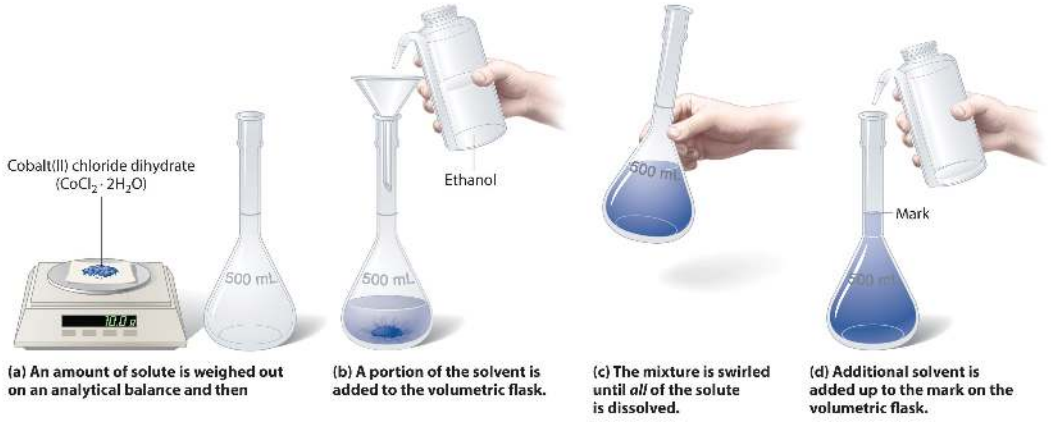


***Figure* 2.1.6.1**: *Preparation of a Solution of Known Concentration Using a Solid Solute*

Example 2.1.6.1: Calculating Moles from Concentration of NaOH

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 2.1.6.3 or Equation 2.1.6.4, 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 2.1.6.3 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 2.1.6.1: Calculating Moles from Concentration of Alanine

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 also often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million* (*ppm*), which is grams of solute per 10^6 g of solution, or in *parts per billion* (*ppb*), which is grams of solute per 10^9 g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table 2.1.6.1.

Table 2.1.6.1: Common Units of Concentration

Concentration	Units
m/m	g of solute/g of solution
m/v	g of solute/mL of solution
ppm	g of solute/10^6 g of solution
	µg/mL
ppb	g of solute/10^9 g of solution
	ng/mL

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 2.1.6.1 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 2.1.6.2, for some substances this effect can be significant, especially for concentrated solutions.

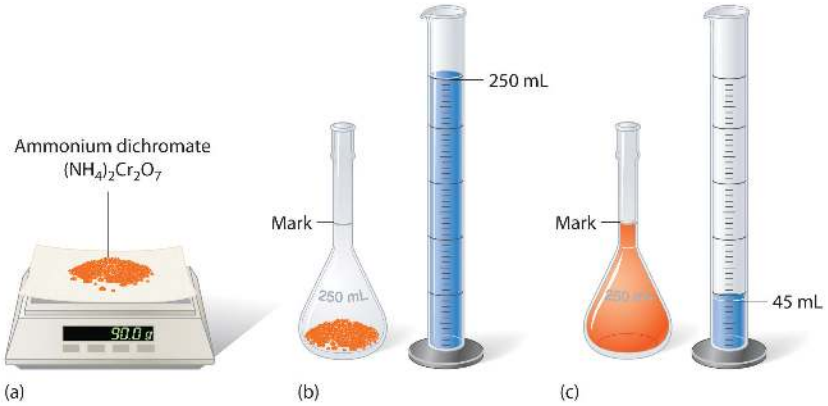


Figure **2.1.6.2**: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

Example 2.1.6.2

The solution contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2$•$2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $\mathbf{CoCl_2 \cdot 2\,H_2O}$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $\mathbf{CoCl_2 \cdot 2\,H_2O}$, 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 $CoCl_2$•$2H_2O$ 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 2.1.6.2

The solution shown in Figure **2.1.6.2** 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 2.1.6.3. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example **2.1.6.3**.

Example 2.1.6.3: D5W Solution

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 2.1.6.3

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 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 2.1.6.3. 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

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{2.1.6.5}$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example 2.1.6.4 demonstrates the calculations involved in diluting a concentrated stock solution.

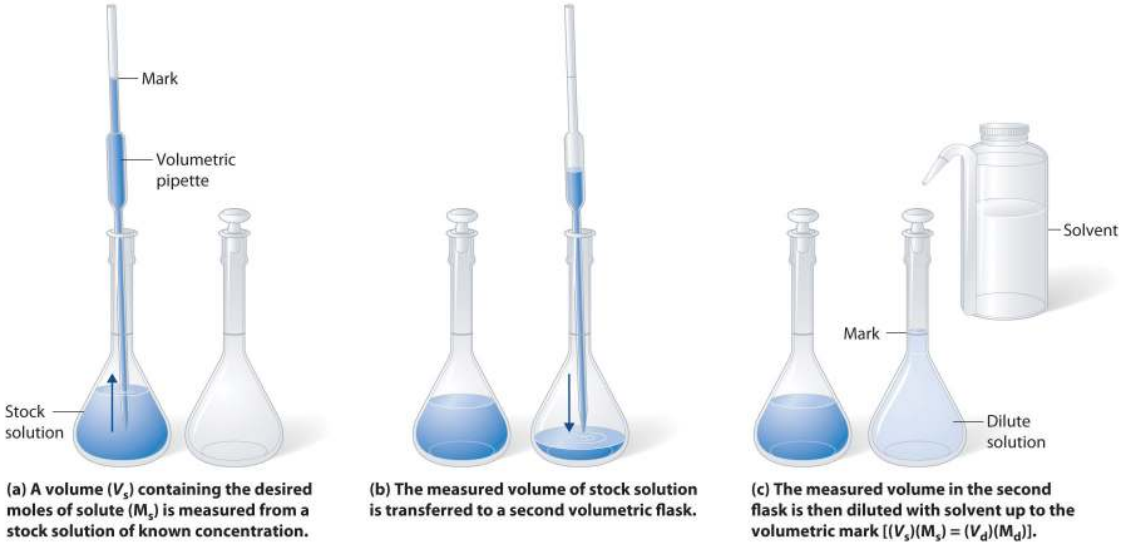


Figure **2.1.6.3**: Preparation of a Solution of Known Concentration by Diluting a Stock Solution. (a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric 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 2.1.6.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example **2.1.6.3**?

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 4.5.3 was 0.310 M glucose. We begin by using Equation 4.5.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$\begin{aligned} moles\ glucose &= 2500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) \\ &= 0.775\ mol\ glucose \end{aligned} \tag{2.1.6.6}$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$\begin{aligned} volume\ of\ stock\ soln &= 0.775\ \cancel{mol\ glucose}\left(\frac{1\ L}{3.00\ \cancel{mol\ glucose}}\right) \\ &= 0.258\ L\ or\ 258\ mL \end{aligned} \tag{2.1.6.7}$$

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).

https://chem.libretexts.org/@go/page/169968

We could also have solved this problem in a single step by solving Equation 4.5.4 for V_s and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500\ L)(0.310\ \cancel{M})}{3.00\ \cancel{M}} = 0.258\ L \tag{2.1.6.8}$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise 2.1.6.4

What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

Answer

16 mL

Ion Concentrations in Solution

In Example **2.1.6.2**, 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:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{2.1.6.9}$$

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 **2.1.6.4**).

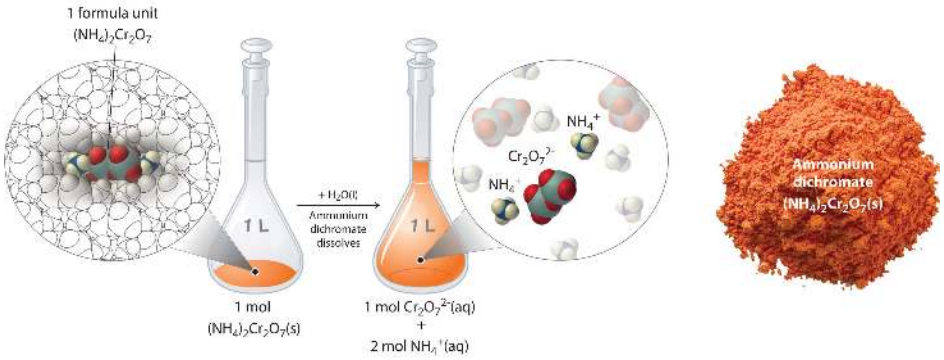


Figure **2.1.6.4**: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

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 2.1.6.5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.21 M NaOH
b. 3.7 M $(CH_3)_2CHOH$
c. 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:

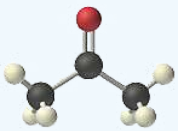
   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   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 2.1.6.5

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



Acetone
$(CH_3)_2CO$

Answer a

$[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$

Answer b

$[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$

Answer c

$[(CH_3)_2CO] = 0.50\ M$

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:**

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{2.1.6.10}$$

- **relationship among volume, molarity, and moles**:

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{2.1.6.11}$$

- **relationship between volume and concentration of stock and dilute solutions**:

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{2.1.6.12}$$

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.

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2.1.7: Solution Stoichiometry and Chemical Analysis

Learning Objectives

- To use titration methods to analyze solutions quantitatively.

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. An expanded version of the flowchart for stoichiometric calculations is shown in Figure **2.1.7.2**. 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, as illustrated in the following examples.

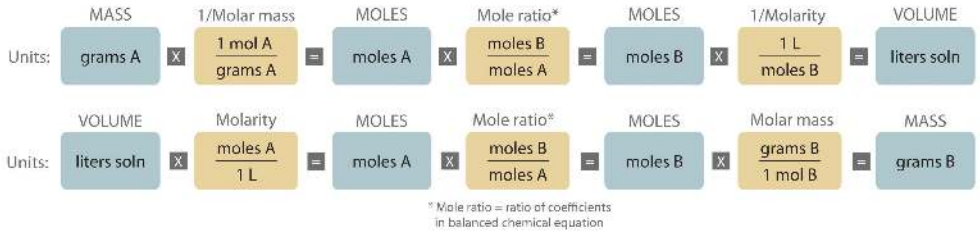


Figure **2.1.7.1**: An Expanded Flowchart for Stoichiometric Calculations. Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

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 2.1.7.1 : 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:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s) \qquad (2.1.7.1)$$

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 **2.1.7.2** is adapted for this particular problem as follows:

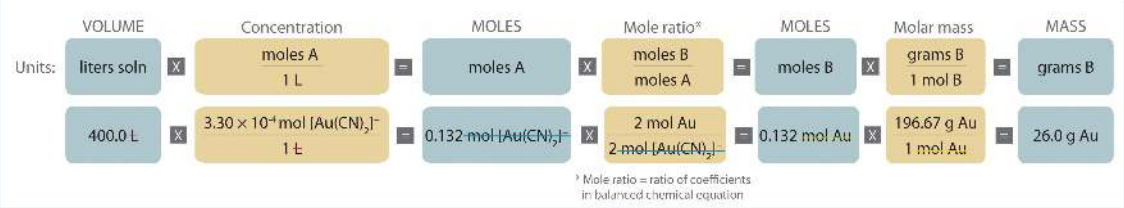


Figure 2.1.7.2: An Expanded Flowchart for the Stoichiometric Calculations.

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:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \tag{2.1.7.2}$$

$$= 400.0\ \cancel{L}\left(\frac{3.30 \times 10^{-4}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \tag{2.1.7.3}$$

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:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \tag{2.1.7.4}$$

$$= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \tag{2.1.7.5}$$

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 2.1.7.1 : Lanthanum Oxalate

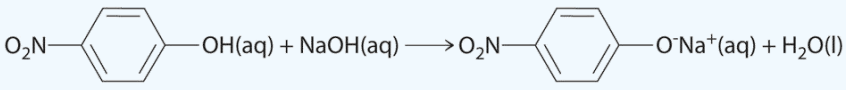
What mass of solid lanthanum(III) oxalate nonahydrate $[La_2(C_2O_4)_3 \cdot 9H_2O]$ can be obtained from 650 mL of a 0.0170 M aqueous solution of $LaCl_3$ by adding a stoichiometric amount of sodium oxalate?

Answer

3.89 g

Exercise 2.1.7.2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



***para*-Nitrophenol** **Yellow**

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 Example **2.1.7.1** and Exercises **2.1.7.1** and **2.1.7.2**, the identities of the limiting reactants are apparent: $[Au(CN)_2]^-$, $LaCl_3$, 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 **2.1.7.2**.

Example 2.1.7.2

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:

$$2\,AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + 2\,KNO_3\,(aq)$$

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). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$K_2Cr_2O_7: \frac{0.085\ mol}{1\ mol} = 0.085$$

$$AgNO_3: \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $AgNO_3$ is the *limiting reactant*.

C Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only 0.14/2 = 0.070 mol of $Ag_2Cr_2O_7$. Finally, convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise 2.1.7.3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2\,NaHCO_3\,(aq) + H_2SO_4\,(aq) \rightarrow 2\,CO_2\,(g) + Na_2SO_4\,(aq) + 2\,H_2O\,(l)$$

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

Determining the Concentration of an Unknown Solution Using a Titration

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. 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 **titration**, a carefully measured volume of a solution of known concentration, called the titrant, 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** is reached when a stoichiometric amount of the titrant has been added—the amount required to react completely with the unknown.

The chemical nature of the species present in the unknown dictates which type of reaction is most appropriate and also how to determine the equivalence point. The volume of titrant added, its concentration, and the coefficients from the balanced chemical equation for the reaction allow us to calculate the total number of moles of the unknown in the original solution. Because we have measured the volume of the solution that contains the unknown, we can calculate the molarity of the unknown substance. This procedure is summarized graphically here:

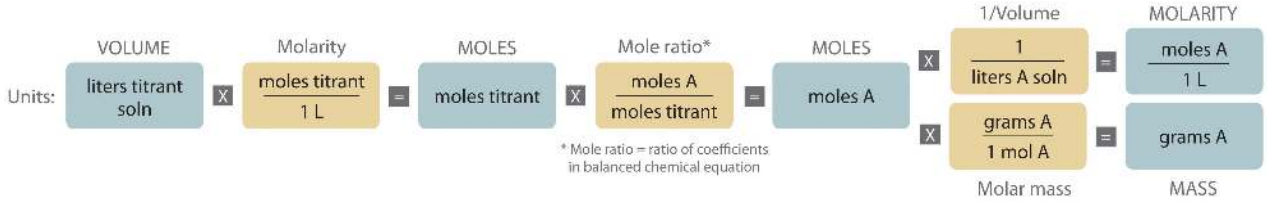


***Figure* 2.1.7.3:** *Dimensional Analysis flowchart for titration problems.*

Example 2.1.7.3: Potassium Permanganate

The calcium salt of oxalic acid [$Ca(O_2CCO_2)$] is found in the sap and leaves of some vegetables, including spinach and rhubarb, and in many ornamental plants. Because oxalic acid and its salts are toxic, when a food such as rhubarb is processed commercially, the leaves must be removed, and the oxalate content carefully monitored.

The reaction of MnO_4^- with oxalic acid (HO_2CCO_2H) in acidic aqueous solution produces Mn^{2+} and CO_2:

$$\underset{\textit{purple}}{MnO_4^-\,(aq)} + HO_2CCO_2H\,(aq) \rightarrow \underset{\textit{colorless}}{Mn^{2+}\,(aq)} + CO_2\,(g) + H_2O\,(l)$$

Because this reaction is rapid and goes to completion, potassium permanganate ($KMnO_4$) is widely used as a reactant for determining the concentration of oxalic acid.

Suppose you stirred a 10.0 g sample of canned rhubarb with enough dilute H_2SO_4(aq) to obtain 127 mL of colorless solution. Because the added permanganate is rapidly consumed, adding small volumes of a 0.0247 M $KMnO_4$ solution, which has a deep purple color, to the rhubarb extract does not initially change the color of the extract. When 15.4 mL of the permanganate solution have been added, however, the solution becomes a faint purple due to the presence of a slight excess of permanganate. If we assume that oxalic acid is the only species in solution that reacts with permanganate, what percentage of the mass of the original sample was calcium oxalate? The video below demonstrates the titration when small, measured amounts of a known permaganate solution are added. At the endpoint, the number of moles of permaganate added equals the number of moles of oxalate in the solution, thus determining how many moles of oxalate we started with.



Given: equation, mass of sample, volume of solution, and molarity and volume of titrant

Asked for: mass percentage of unknown in sample

Strategy:

A. Balance the chemical equation for the reaction using oxidation states.

B. Calculate the number of moles of permanganate consumed by multiplying the volume of the titrant by its molarity. Then calculate the number of moles of oxalate in the solution by multiplying by the ratio of the coefficients in the balanced chemical equation. Because calcium oxalate contains a 1:1 ratio of Ca^{2+}:$^{-}O_2CCO_2^{-}$, the number of moles of oxalate in the solution is the same as the number of moles of calcium oxalate in the original sample.

C. Find the mass of calcium oxalate by multiplying the number of moles of calcium oxalate in the sample by its molar mass. Divide the mass of calcium oxalate by the mass of the sample and convert to a percentage to calculate the percentage by mass of calcium oxalate in the original sample.

Solution:

A As in all other problems of this type, the first requirement is a balanced chemical equation for the reaction. Using oxidation states gives

$$\begin{aligned} &2MnO_4^-(aq) + 5HO_2CCO_2H(aq) + 6H^+(aq) \\ &\rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \end{aligned} \tag{2.1.7.6}$$

Thus each mole of MnO_4^- added consumes 2.5 mol of oxalic acid.

B Because we know the concentration of permanganate (0.0247 M) and the volume of permanganate solution that was needed to consume all the oxalic acid (15.4 mL), we can calculate the number of moles of MnO_4^- consumed. To do this we first convert the volume in mL to a volume in liters. Then simply multiplying the molarity of the solution by the volume in liters we find the number of moles of MnO_4^-

$$15.4 \cancel{mL} \left(\frac{1 \cancel{L}}{1000 \cancel{mL}} \right) \left(\frac{0.0247 \; mol \; MnO_4^-}{1 \cancel{L}} \right) = 3.80 \times 10^4 \; mol \; MnO_4^- \tag{2.1.7.7}$$

The number of moles of oxalic acid, and thus oxalate, present can be calculated from the mole ratio of the reactants in the balanced chemical equation. We can abbreviate the table needed to calculate the number of moles of oxalic acid in the

$$moles \; HO_2CCO_2H = 3.80 \times 10^{-4} \; \cancel{mol \; MnO_4^-} \left(\frac{5 \; mol \; HO_2CCO_2H}{2 \; \cancel{mol \; MnO_4^-}} \right) \tag{2.1.7.8}$$

$$= 9.50 \times 10^{-4} \; mol \; HO_2CCO_2H \tag{2.1.7.9}$$

C The problem asks for the *percentage* of calcium oxalate by mass in the original 10.0 g sample of rhubarb, so we need to know the mass of calcium oxalate that produced 9.50×10^{-4} mol of oxalic acid. Because calcium oxalate is $Ca(O_2CCO_2)$, 1 mol of calcium oxalate gave 1 mol of oxalic acid in the initial acid extraction:

$$Ca(O_2CCO_2)(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + HO_2CCO_2H(aq) \quad (2.1.7.10)$$

The mass of calcium oxalate originally present was thus

$$mass\ of\ CaC_2O_4 = 9.50 \times 10^{-4}\ \cancel{mol\ HO_2CCO_2H} \left(\frac{1\ \cancel{mol\ CaC_2O_4}}{1\ \cancel{mol\ HO_2CCO_2H}}\right)\left(\frac{128.10\ g\ CaC_2O_4}{1\ \cancel{mol\ CaC_2O_4}}\right) \quad (2.1.7.11)$$

$$= 0.122\ g\ CaC_2O_4 \quad (2.1.7.12)$$

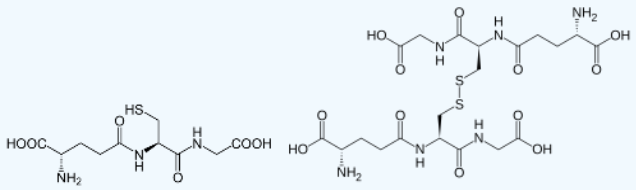
The original sample contained 0.122 g of calcium oxalate per 10.0 g of rhubarb. The percentage of calcium oxalate by mass was thus

$$\%CaC_2O_4 = \frac{0.122\ g}{10.0\ g} \times 100 = 1.22\% \quad (2.1.7.13)$$

Because the problem asked for the percentage by mass of calcium oxalate in the original sample rather than for the *concentration* of oxalic acid in the extract, we do not need to know the volume of the oxalic acid solution for this calculation.

Exercise 2.1.7.4: Glutathione

Glutathione is a low-molecular-weight compound found in living cells that is produced naturally by the liver. Health-care providers give glutathione intravenously to prevent side effects of chemotherapy and to prevent kidney problems after heart bypass surgery. Its structure is as follows:



Glutathione is found in two forms: one abbreviated as (left) GSH (indicating the presence of an –SH group) and the other (right) as GSSG (the *disulfide* form, in which an S–S bond links two glutathione units). The GSH form is easily oxidized to GSSG with elemental iodine:

$$2\,GSH\,(aq) + I_2\,(aq) \rightarrow GSSG\,(aq) + 2\,HI\,(aq)$$

A small amount of soluble starch is added as an indicator. Because starch reacts with excess I_2 to give an intense blue color, the appearance of a blue color indicates that the equivalence point of the reaction has been reached.

Adding small volumes of a 0.0031 M aqueous solution of I_2 to 194 mL of a solution that contains glutathione and a trace of soluble starch initially causes no change. After 16.3 mL of iodine solution have been added, however, a permanent pale blue color appears because of the formation of the starch-iodine complex. What is the concentration of glutathione in the original solution?

Answer

5.2×10^{-4} M

Standard Solutions

In Exercise 2.1.7.4, the concentration of the titrant (I_2) was accurately known. The accuracy of any titration analysis depends on an accurate knowledge of the concentration of the titrant. Most titrants are first *standardized*; that is, their concentration is measured by titration with a standard solution, which is a solution whose concentration is known precisely. Only pure crystalline compounds that do not react with water or carbon dioxide are suitable for use in preparing a standard solution. One such compound is potassium hydrogen phthalate (KHP), a weak monoprotic acid suitable for standardizing solutions of bases such as sodium hydroxide. The reaction of KHP with NaOH is a simple acid–base reaction. If the concentration of the KHP solution is known accurately and the titration of a NaOH solution with the KHP solution is carried out carefully, then the concentration of the NaOH solution can be calculated precisely. The standardized NaOH solution can then be used to titrate a solution of an acid whose concentration is unknown.

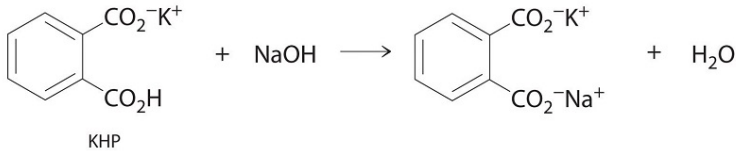


Figure 2.1.7.4: The reaction of KHP with NaOH. As with all acid-base reactions, a salt is formed.

Acid–Base Titrations

Because most common acids and bases are not intensely colored, a small amount of an acid–base **indicator** is usually added to detect the equivalence point in an acid–base titration. The point in the titration at which an indicator changes color is called the endpoint (the point in a titration at which an indicator changes color). The procedure is illustrated in Example **2.1.7.4**.

Example 2.1.7.4: Vitamin C

The structure of vitamin C (ascorbic acid, a monoprotic acid) is as follows:

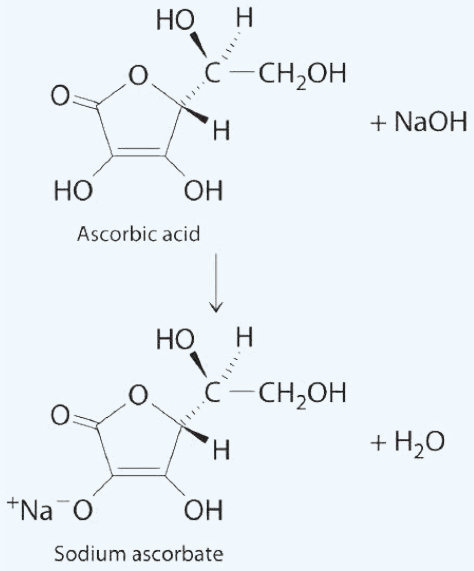


Figure 2.1.7.5: Ascorbic acid. *The upper figure shows the three-dimensional representation of ascorbic acid. Hatched lines indicate bonds that are behind the plane of the paper, and wedged lines indicate bonds that are out of the plane of the paper.*

An absence of vitamin C in the diet leads to the disease known as scurvy, a breakdown of connective tissue throughout the body and of dentin in the teeth. Because fresh fruits and vegetables rich in vitamin C are readily available in developed countries today, scurvy is not a major problem. In the days of slow voyages in wooden ships, however, scurvy was common. Ferdinand Magellan, the first person to sail around the world, lost more than 90% of his crew, many to scurvy. Although a diet rich in fruits and vegetables contains more than enough vitamin C to prevent scurvy, many people take supplemental doses of vitamin C, hoping that the extra amounts will help prevent colds and other illness.

Suppose a tablet advertised as containing 500 mg of vitamin C is dissolved in 100.0 mL of distilled water that contains a small amount of the acid–base indicator bromothymol blue, an indicator that is yellow in acid solution and blue in basic solution, to give a yellow solution. The addition of 53.5 mL of a 0.0520 M solution of NaOH results in a change to green at the endpoint, due to a mixture of the blue and yellow forms of the indicator. What is the actual mass of vitamin C in the tablet? (The molar mass of ascorbic acid is 176.13 g/mol.)



Figure 2.1.7.6: Bromothymol Blue is used as an indicator. If placed in a acidic solution it will turn the solution yellow, and if placed in a basic solution it will turn the solution blue. The equivalence point is seen when the solution turns green. pH is important for a variety of reasons. For example if you are trying to discard an acidic solution, you could add bromothymol blue to the solution and then titrate in some base until the solution turned green. This indicates that it is neutral. Image from The Science Education Resources Center at Carleton.

Given: reactant, volume of sample solution, and volume and molarity of titrant

Asked for: mass of unknown

Strategy:

A Write the balanced chemical equation for the reaction and calculate the number of moles of base needed to neutralize the ascorbic acid.

B Using mole ratios, determine the amount of ascorbic acid consumed. Calculate the mass of vitamin C by multiplying the number of moles of ascorbic acid by its molar mass.

Solution:

A Because ascorbic acid acts as a monoprotic acid, we can write the balanced chemical equation for the reaction as

$$HAsc(aq) + OH^-(aq) \rightarrow Asc^-(aq) + H_2O(l) \tag{2.1.7.14}$$

where HAsc is ascorbic acid and Asc^- is ascorbate. The number of moles of OH^- ions needed to neutralize the ascorbic acid is

$$\begin{aligned} moles\ OH^- &= 53.5\ \cancel{mL}\left(\frac{\cancel{1\ L}}{1000\ \cancel{mL}}\right)\left(\frac{0.0520\ mol\ OH^-}{\cancel{1\ L}}\right) \\ &= 2.78 \times 10^{-3}\ mol\ OH^- \end{aligned} \tag{2.1.7.15}$$

B The mole ratio of the base added to the acid consumed is 1:1, so the number of moles of OH^- added equals the number of moles of ascorbic acid present in the tablet:

$$\begin{aligned} mass\ ascorbic\ acid \\ = 2.78 \times 10^{-3}\ \cancel{mol\ HAsc}\left(\frac{176.13\ g\ HAsc}{1\ \cancel{mol\ HAsc}}\right) &= 0.490\ g\ HAsc \end{aligned} \tag{2.1.7.16}$$

Because 0.490 g equals 490 mg, the tablet contains about 2% less vitamin C than advertised.

Exercise 2.1.7.5: Vinegar

Vinegar is essentially a dilute solution of acetic acid in water. Vinegar is usually produced in a concentrated form and then diluted with water to give a final concentration of 4%–7% acetic acid; that is, a 4% m/v solution contains 4.00 g of acetic acid per 100 mL of solution. If a drop of bromothymol blue indicator is added to 50.0 mL of concentrated vinegar stock and 31.0 mL of 2.51 M NaOH are needed to turn the solution from yellow to green, what is the percentage of acetic acid in the vinegar stock? (Assume that the density of the vinegar solution is 1.00 g/mL.)

Answer

9.35%

Summary

Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation. 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.

Quantitative analysis of an unknown solution can be achieved using titration methods. The concentration of a species in solution can be determined by **quantitative analysis**. One such method is a **titration**, in which a measured volume of a solution of one substance, the **titrant**, is added to a solution of another substance to determine its concentration. The **equivalence point** in a titration is the point at which exactly enough reactant has been added for the reaction to go to completion. A **standard solution**, a solution whose concentration is known precisely, is used to determine the concentration of the titrant. Many titrations, especially those that involve acid–base reactions, rely on an indicator. The point at which a color change is observed is the **endpoint**, which is close to the equivalence point if the indicator is chosen properly.

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SECTION OVERVIEW

Topic C- Gas Laws and Kinetic Molecular Theory

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

1. Use classical gas laws to relate changes in pressure, volume, temperature, and number of moles to one another.
2. Use Dalton's Law of Partial Pressures to solve problems involving mixtures of gases.
3. Use vapor pressure information and the classical gas laws to describe the behavior of a gas when it is collected over water.
4. Solve stoichiometry problems involving gases, using the ideal gas law.
5. Have sufficient understanding of basic kinetic theory to be able to:
    a. Solve problems involving kinetic energy, temperature, molar mass, and particle velocity for an ideal gas.
    b. Use effusion rates to determine the molar mass of a gas.
    c. Answer qualitative questions about the Boltzmann distribution of kinetic energies and velocities, and their relationships to temperature and molar mass.
6. Describe the factors that differentiate real gas behavior from the ideal gas model, and use the van der Waals equation to model real gas behavior.

3.1: Gases

3.1.1: Characteristics of Gases
3.1.2: Pressure
3.1.3: The Gas Laws
3.1.4: The Ideal Gas Equation
3.1.5: Gas Volumes and Chemical Reactions
3.1.6: Gas Mixtures and Partial Pressures
3.1.7: Partial Pressures and Stoichiometry
3.1.8: Kinetic-Molecular Theory
3.1.9: Understanding the Value Distribution of a Variable
3.1.10: Molecular Speed Distribution
3.1.11: Kinetic Energy Distribution
3.1.12: Molecular Effusion and Diffusion
3.1.13: Real Gases - Deviations from Ideal Behavior

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CHAPTER OVERVIEW

3.1: Gases

Previously, we focused on the *microscopic* properties of matter—the properties of individual atoms, ions, and molecules—and how the electronic structures of atoms and ions determine the stoichiometry and three-dimensional geometry of the compounds they form. We will now focus on *macroscopic* properties—the behavior of aggregates with large numbers of atoms, ions, or molecules. An understanding of macroscopic properties is central to an understanding of chemistry. Why, for example, are many substances gases under normal pressures and temperatures (1.0 atm, 25°C), whereas others are liquids or solids? We will examine each form of matter—gases, liquids, and solids—as well as the nature of the forces, such as hydrogen bonding and electrostatic interactions, that hold molecular and ionic compounds together in these three states.

In this chapter, 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.

3.1.1: Characteristics of Gases
3.1.2: Pressure
3.1.3: The Gas Laws
3.1.4: The Ideal Gas Equation
3.1.5: Gas Volumes and Chemical Reactions
3.1.6: Gas Mixtures and Partial Pressures
3.1.7: Partial Pressures and Stoichiometry
3.1.8: Kinetic-Molecular Theory
3.1.9: Understanding the Value Distribution of a Variable
3.1.10: Molecular Speed Distribution
3.1.11: Kinetic Energy Distribution
3.1.12: Molecular Effusion and Diffusion
3.1.13: Real Gases - Deviations from Ideal Behavior

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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3.1.1: Characteristics 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 **3.1.1.1** compares the three states of matter and illustrates the differences at the molecular level.

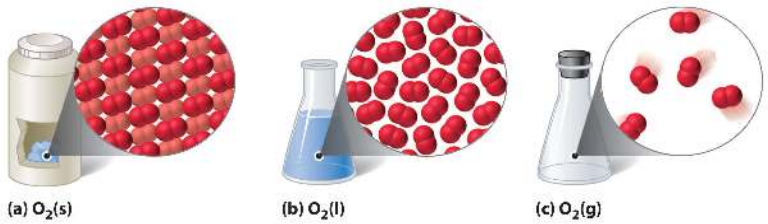


Figure **3.1.1.1**: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (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 10.1.

Table **3.1.1.1**: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm3)
≤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 **3.1.1.2** 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.

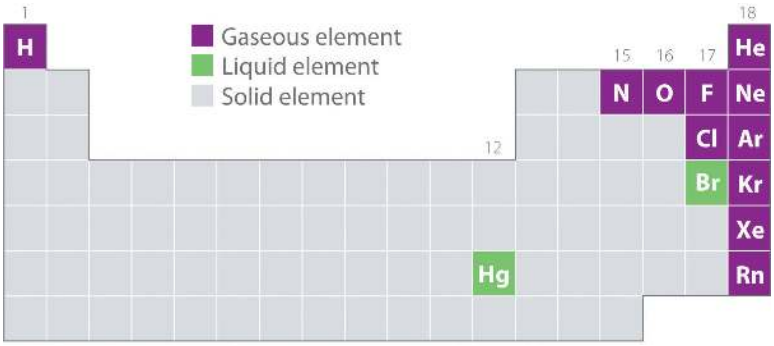


Figure **3.1.1.2**: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

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.

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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3.1.2: 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:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{3.1.2.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 3.1.2.1 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):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{3.1.2.2}$$

Example 3.1.2.1

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 3.1.2.1 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 3.1.2.1

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 **3.1.2.1**). 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:

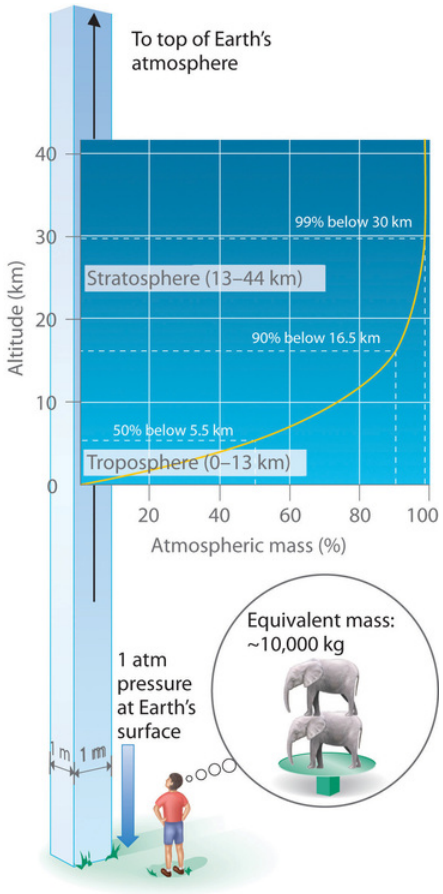


Figure **3.1.2.1**: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

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 **3.1.2.2**). 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:

$$P = \frac{F}{A} \tag{3.1.2.3}$$

$$= \frac{mg}{A} \tag{3.1.2.4}$$

$$= \frac{\rho V \cdot g}{A} \tag{3.1.2.5}$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \tag{3.1.2.6}$$

$$= \rho gh \tag{3.1.2.7}$$

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 3.1.2.2. 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.

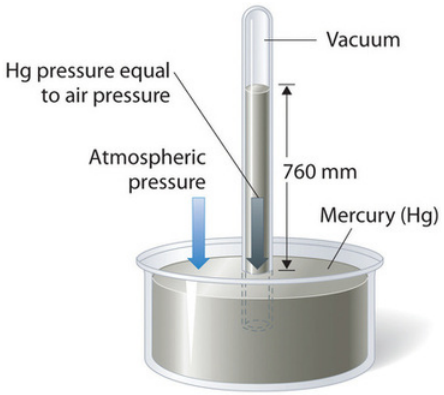


Figure 3.1.2.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the 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:

$$1\ \text{atm} = 760\ mmHg \tag{3.1.2.8}$$
$$= 760\ torr \tag{3.1.2.9}$$
$$= 1.01325 \times 10^5\ Pa \tag{3.1.2.10}$$
$$= 101.325\ kPa \tag{3.1.2.11}$$

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 3.1.2.2: 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 3.1.2.11 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 3.1.2.11, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{3.1.2.12}$$
$$= 0.597 \text{ atm}$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{3.1.2.13}$$
$$= 0.605 \text{ bar}$$

Exercise 3.1.2.2: 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 3.1.2.3. 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.

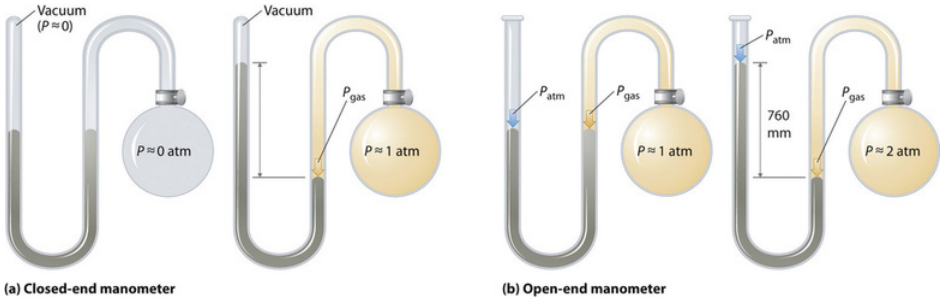


Figure 3.1.2.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) 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 3.1.2.3, 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 3.1.2.3

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

$$P = 0.200\ \text{atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 152\ \text{mmHg} \tag{3.1.2.14}$$

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

$$P = \rho_{\text{wat}} g h_{\text{wat}} = \rho_{\text{Hg}} g h_{\text{Hg}} \tag{3.1.2.15}$$

$$h_{\text{wat}} = h_{\text{Hg}} \times \frac{\rho_{\text{Hg}}}{\rho_{\text{wat}}} = 152\ \text{mm} \times \frac{13.53\ \text{g/cm}^3}{1.00\ \text{g/cm}^3} = 2070\ \text{mm} \tag{3.1.2.16}$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise 3.1.2.3

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

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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3.1.3: The Gas Laws

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.

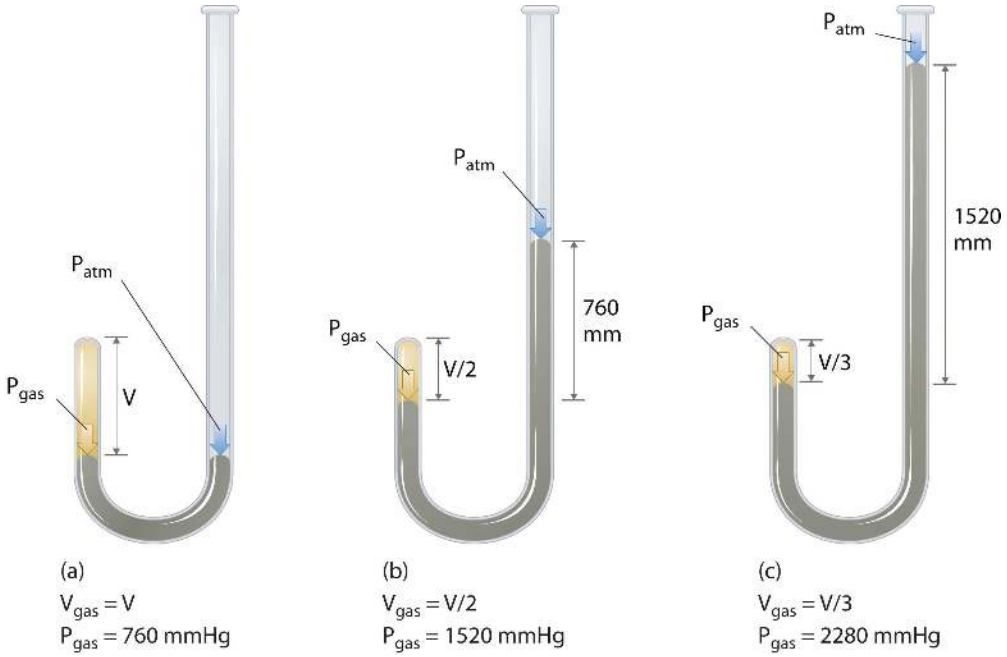


Figure 3.1.3.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is 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 $V/3$ (CC BY-SA-NC; anonymous by request).

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 3.1.3.1. 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 3.1.3.2). 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:

$$PV = \text{constant} \tag{3.1.3.1}$$

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{3.1.3.2}$$

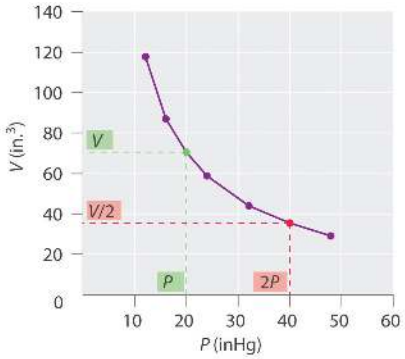
or

$$V \propto \frac{1}{P} \tag{3.1.3.3}$$

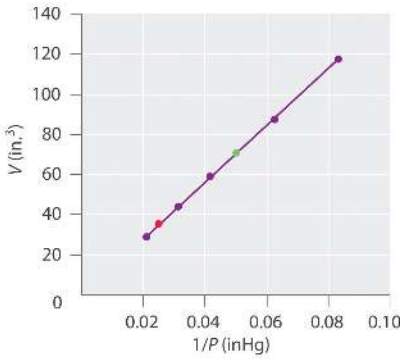
where the ∝ symbol is read "is proportional to." A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equations 3.1.3.1 and 3.1.3.3. Dividing both sides of Equation 3.1.3.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the 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.* This law in practice is shown in Figure **3.1.3.2**.

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 **3.1.3.2**: 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 (CC BY-SA-NC; anonymous by request).

> *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure*

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 **3.1.3.3**).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 **3.1.3.3** 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 **3.1.3.3**, 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.

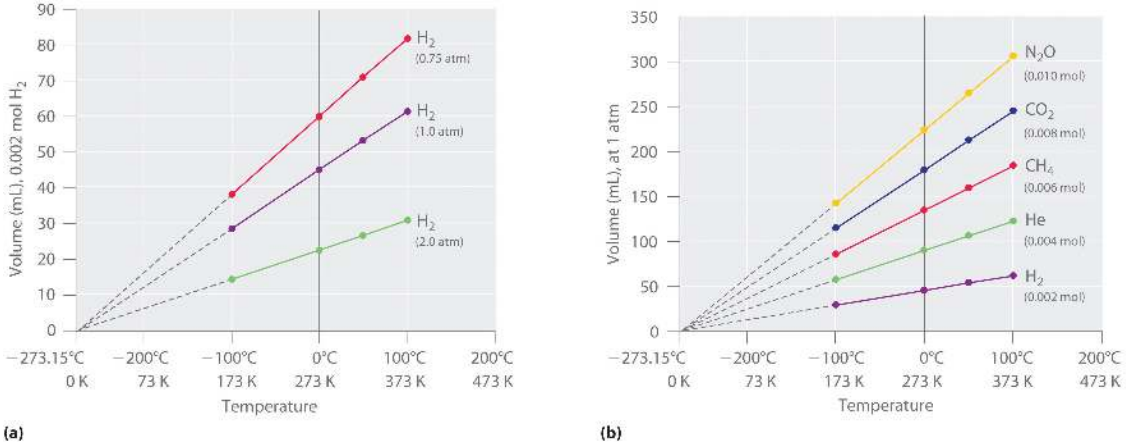


Figure **3.1.3.3**: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data 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 (CC BY-SA-NC; anonymous by request).

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 **3.1.3.3** is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\, T \tag{3.1.3.4}$$

or

$$V \propto T \tag{3.1.3.5}$$

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.

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 **3.1.3.4**). This is the historic "Avogadro's hypothesis."

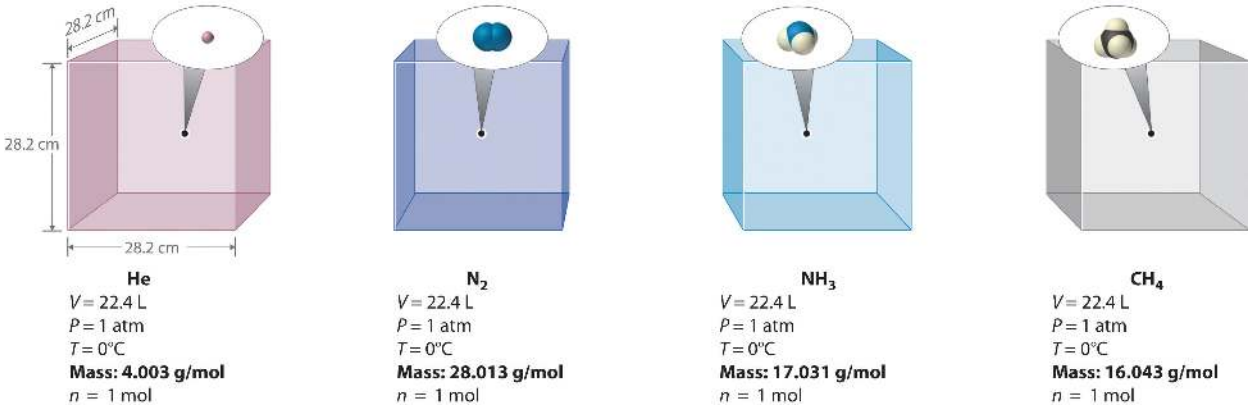


Figure **3.1.3.4**: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous by request).

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,

$$V = \text{const.}\ (n) \tag{3.1.3.6}$$

or

$$V \propto .n@\ \text{constant T and P} \tag{3.1.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

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 **3.1.3.5**. Volume *increases* with increasing temperature or amount, but *decreases* with increasing pressure.



Figure **3.1.3.5**: 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 (CC BY-SA-NC; anonymous by request).

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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3.1.4: The Ideal Gas Equation

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 were derived previously:

- **Boyle's law**

$$V \propto \frac{1}{P} \text{ @ constant n and T} \tag{3.1.4.1}$$

- **Charles's law**

$$V \propto T \text{ @ constant n and P} \tag{3.1.4.2}$$

- **Avogadro's law**

$$V \propto n \text{ @ constant T and P} \tag{3.1.4.3}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{3.1.4.4}$$

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

$$V = \text{Cons.}\left(\frac{nT}{P}\right) \tag{3.1.4.5}$$

By convention, the proportionality constant in Equation 3.1.4.4 is called the gas constant, which is represented by the letter R. Inserting R into Equation 3.1.4.5 gives

$$V = \frac{RnT}{P} = \frac{nRT}{P} \tag{3.1.4.6}$$

Clearing the fractions by multiplying both sides of Equation 3.1.4.7 by P gives

$$PV = nRT \tag{3.1.4.7}$$

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.

> *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

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{3.1.4.8}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{3.1.4.9}$$

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 $1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$ pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ bar} = 10^5 \text{ Pa} \tag{3.1.4.10}$$

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 3.1.4.7:

$$V = \frac{nRT}{P} \tag{3.1.4.11}$$

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 **3.1.4.1**: 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 3.1.4.1

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 3.1.4.7) for *n*, we obtain

$$745\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.980\ \text{atm} \tag{3.1.4.12}$$

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:

$$T = 273 + 30 = 303\text{K} \tag{3.1.4.13}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980\ \text{atm} \times 31150\ \text{L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303\ \text{K}} = 1.23 \times 10^3\ \text{mol} \tag{3.1.4.14}$$

Exercise 3.1.4.1

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 **3.1.4.1**, 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 **3.1.4.5**.

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:

$$\begin{matrix} \textbf{Initial condition } (i) & \textbf{Final condition} (f) \\ P_i V_i = n_i R T_i & P_f V_f = n_f R T_f \end{matrix} \tag{3.1.4.15}$$

Both equations can be rearranged to give:

$$R = \frac{P_i V_i}{n_i T_i} \qquad R = \frac{P_f V_f}{n_f T_f} \tag{3.1.4.16}$$

The two equations are equal to each other since each is equal to the same constant ***R***. Therefore, we have:

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f} \tag{3.1.4.17}$$

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 3.1.4.2

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 **3.1.4.1**?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example **3.1.4.1** 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)
$T_i = 30\,°C = 303\,K$	$T_f = -10°C = 263\,K$
$P_i = 0.980\,atm$	$P_f = 0.980\,atm$
$n_i = 1.23 \times 10^3\,mol$	$n_f = 1.23 \times 10^3\,mol$
$V_i = 31150\,L$	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:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{3.1.4.18}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} = 2.70 \times 10^4\ \text{L} \tag{3.1.4.19}$$

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 3.1.4.2

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 **3.1.4.1** 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 **3.1.4.1** can be applied in *any* such case, as we demonstrate in Example **3.1.4.2** (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 3.1.4.3

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 **3.1.4.2**.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Initial	Final
$V_i = 0.406\ \text{L}$	$V_f = 0.406\ \text{L}$
$n_i = 0.025\ \text{mol}$	$n_f = 0.025\ \text{mol}$
$T_i = 25\ ^\circ\text{C} = 298\ \text{K}$	$T_f = 750\ ^\circ\text{C} = 1023\ \text{K}$
$P_i = 1.5\ \text{atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f} \tag{3.1.4.20}$$

By solving the equation for P_f, we get:

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 1.5\ \text{atm} \times \frac{1023\ \text{K}}{298\ \text{K}} \\ &= 5.1\ atm \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Exercise 3.1.4.3

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 Examples **3.1.4.1** and **3.1.4.2**, 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 3.1.4.4

We saw in Example **3.1.4.1** 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 **3.1.4.3**.

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 3.1.4.17 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{3.1.4.21}$$

By solving the equation for V_f, we get:

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} = 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}} = 5.96 \times 10^4\ \text{L} \tag{3.1.4.22}$$

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 3.1.4.4

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

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

$$\frac{n}{V} = \frac{P}{RT} \tag{3.1.4.23}$$

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):

$$n = \frac{m}{M} \tag{3.1.4.24}$$

Substituting this expression for n into Equation 3.1.4.23 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{3.1.4.25}$$

Because m/V is the density ρ of a substance, we can replace m/V by ρ and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{3.1.4.26}$$

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 3.1.4.5

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 3.1.4.26 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol} \tag{3.1.4.27}$$

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:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm} \tag{3.1.4.28}$$

B Substituting these values into Equation 3.1.4.26 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L} \tag{3.1.4.29}$$

Exercise 3.1.4.5

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 3.1.4.26 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 3.1.4.6.

Example 3.1.4.6

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 3.1.4.26 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 3.1.4.26 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{3.1.4.30}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L} \tag{3.1.4.31}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K \tag{3.1.4.32}$$

$$P = 727\text{mmHg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm} \tag{3.1.4.33}$$

The molar mass of the unknown gas is thus

$$M = \frac{1.84\text{ g/L} \times 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol} \tag{3.1.4.34}$$

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:

$$M(\mathrm{NO}) = 14 + 16 = 30\ \mathrm{g/mol} \tag{3.1.4.35}$$

$$M(\mathrm{N_2O}) = (2)(14) + 16 = 44\ \mathrm{g/mol} \tag{3.1.4.36}$$

$$M(\mathrm{NO_2}) = 14 + (2)(16) = 46\ \mathrm{g/mol} \tag{3.1.4.37}$$

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 3.1.4.6

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

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 $R = 0.08206 \frac{\mathrm{L \cdot atm}}{\mathrm{K \cdot mol}} = 8.3145 \frac{\mathrm{J}}{\mathrm{K \cdot mol}}$

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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3.1.5: Gas Volumes and Chemical Reactions

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.

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.

Gas Volumes in Chemical Reactions

The ideal gas law can be used to calculate volume of gases consumed or produced. The ideal-gas equation frequently is used to interconvert between volumes and molar amounts in chemical equations.

Example 3.1.5.2A

What volume of carbon dioxide gas is produced at STP by the decomposition of 0.150 g $\mathbf{CaCO_3}$ via the equation:

$$\mathbf{CaCO_3\,(s)\ \rightarrow CaO\,(s) + CO_2\,(g)}$$

Solution

Begin by converting the mass of calcium carbonate to moles.

$$\frac{0.150\ g}{100.1\ g/mol} = 0.00150\ mol$$

The stoichiometry of the reaction dictates that the number of moles $\mathbf{CaCO_3}$ decomposed equals the number of moles $\mathbf{CO_2}$ produced. Use the ideal-gas equation to convert moles of $\mathbf{CO_2}$ to a volume.

$$\begin{aligned} V &= \frac{nRT}{PR} \\ &= \frac{(0.00150\ mol)\left(0.08206\ \frac{L \cdot atm}{mol \cdot K}\right)(273.15\ K)}{1\ atm} \\ &= 0.0336\ L\ or\ 33.6\ mL \end{aligned}$$

Example 3.1.5.2B

A 3.00 L container is filled with $\mathbf{Ne\,(g)}$ at 770 mmHg at 27°C. A **0.633 g** sample of $\mathbf{CO_2}$ vapor is then added.

- What is the partial pressure of $\mathbf{CO_2}$ and **Ne** in atm?
- What is the total pressure in the container in atm?

Solution

Step 1: Write down all given information, and convert as necessary.

Before:

- \(P = 770\,mmHg \rigtharrow 1.01 \,atm\]
- $V = 3.00\,L$
- $n_{Ne} = ?$

- $T = 27°C \rightarrow 300\ K$

Other Unknowns: n_{CO_2}= ?

$$n_{CO_2} = 0.633\ \text{g CO}_2 \times \frac{1\ \text{mol}}{44\ \text{g}} = 0.0144\ \text{mol CO}_2$$

Step 2: After writing down all your given information, find the unknown moles of **Ne**.

$$\begin{aligned} n_{Ne} &= \frac{PV}{RT} \\ &= \frac{(1.01\ \text{atm})(3.00\ \text{L})}{(0.08206\ atm\ L/mol\ K)(300\ \text{K})} \\ &= 0.123\ \text{mol} \end{aligned}$$

Because the pressure of the container before the CO_2 was added contained only **Ne**, that is your partial pressure of *Ne*. After converting it to atm, you have already answered part of the question!

$$P_{Ne} = 1.01\ \text{atm}$$

Step 3: Now that have pressure for **Ne**, you must find the partial pressure for CO_2. Use the ideal gas equation.

$$\frac{P_{Ne}\cancel{V}}{n_{Ne}\cancel{RT}} = \frac{P_{CO_2}\cancel{V}}{n_{CO_2}\cancel{RT}}$$

but because both gases share the same Volume (V) and Temperature (T) and since the Gas Constant (R) is constants, all three terms cancel.

$$\begin{aligned} \frac{P}{n_{Ne}} &= \frac{P}{n_{CO_2}} \\ \frac{1.01\ \text{atm}}{0.123\ \text{mol Ne}} &= \frac{P_{CO_2}}{0.0144\ \text{mol CO}_2} \\ P_{CO_2} &= 0.118\ \text{atm} \end{aligned}$$

This is the partial pressure CO_2.

Step 4: Now find total pressure.

$$\begin{aligned} P_{total} &= P_{Ne} + P_{CO_2} \\ &= 1.01\ \text{atm} + 0.118\ \text{atm} \\ &= 1.128\ \text{atm} \\ &\approx 1.13\ \text{atm (with appropriate significant figures)} \end{aligned}$$

Example 3.1.5.2*C*: Sulfuric Acid

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:

$$2\,S\,(s) + 3\,O_2\,(g) + 2\,H_2O\,(l) \rightarrow 2\,H_2SO_4\,(aq)$$

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:

$$\text{mass of } H_2SO_4 \rightarrow \text{moles } H_2SO_4 \rightarrow \text{moles } O_2 \rightarrow \text{liters } O_2$$

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3 \text{mol } O_2}{2 \text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} \\ &= 3.43 \times 10^5 \ L \end{aligned}$$

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 3.1.5.2

Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

$$Fe(s) + 2\,HCl(aq) \rightarrow H_2(g) + FeCl_2(aq)$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature were 30°C and the atmospheric pressure was 745 mmHg?

Answer

68.6 kg of Fe (approximately 150 lb)

Example 3.1.5.3: Emergency Air bags

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2\,NaN_3 \rightarrow 2\,Na(s) + 3\,N_2(g)$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, 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 $\mathbf{N_2}$ gas produced. From the data in Table S3, determine the partial pressure of $\mathbf{N_2}$ gas in the flask.

B Use the ideal gas law to find the volume of $\mathbf{N_2}$ 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 $\mathbf{N_2}$ gas produced:

$$\frac{5.00\ \text{g NaN}_3}{(22.99 + 3 \times 14.01)\ \text{g/mol}} \times \frac{3\text{mol N}_2}{2\text{mol NaN}_3} = 0.115\ \text{mol N}_2$$

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 S3 tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the $\mathbf{N_2}$ gas in the flask is only

$$(762 - 18.65)\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 743.4\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}}$$

$$= 0.978\ atm.$$

B Solving the ideal gas law for V and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L}$$

Exercise 3.1.5.3

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce $\mathbf{H_2}$ gas according to the equation

$$\text{Zn}(s) + 2\,\text{HCl}(aq) \longrightarrow \text{H}_2(g) + \text{ZnCl}_2(aq).$$

The resulting H_2 gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer

0.397 L

Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

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3.1.6: Gas Mixtures and Partial Pressures

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:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{3.1.6.1}$$

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

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{3.1.6.2}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

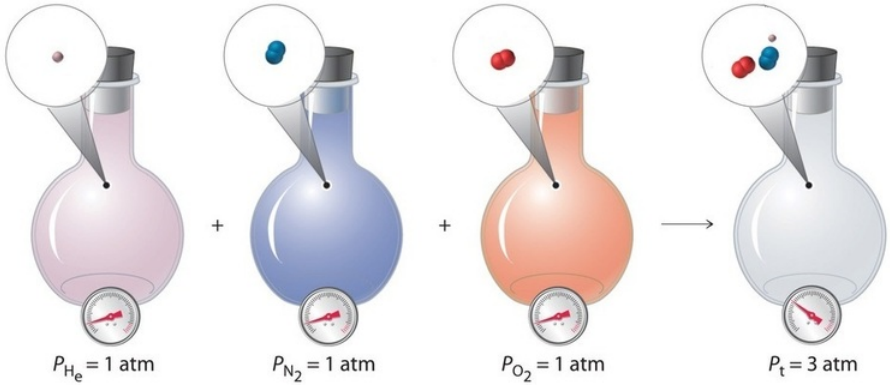


Figure 3.1.6.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{3.1.6.3}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{3.1.6.4}$$

$$P_{tot} = \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{3.1.6.5}$$

Equation 3.1.6.5 restates Equation 3.1.6.3 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 3.1.6.5 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 **3.1.6.1**.

Example 3.1.6.1: The Bends

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

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol} \tag{3.1.6.6}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol} \tag{3.1.6.7}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm} \tag{3.1.6.8}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm} \tag{3.1.6.9}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm} \tag{3.1.6.10}$$

Exercise 3.1.6.1

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}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{3.1.6.11}$$

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

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{3.1.6.12}$$

Rearranging this equation gives

$$P_A = x_A P_{tot} \tag{3.1.6.13}$$

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 10.6.7, 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 3.1.6.2: Exhaling Composition

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 3.1.6.13.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{3.1.6.14}$$

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:

$$x_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063 \tag{3.1.6.15}$$

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 3.1.6.2

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

$$P_{CO_2} = 86 \text{ atm} \tag{3.1.6.16}$$

$$P_{N_2} = 2.7 \text{ atm} \tag{3.1.6.17}$$

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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3.1.7: Partial Pressures and Stoichiometry

Learning Objectives

- To solve stoichiometry problems involving mixtures of gases.

In our use of Dalton's Law thus far, we have focused entirely on inert gas mixtures where no chemical reaction occurs. But what happens when two or more gases are mixed and they react? In this section, we describe how to solve stoichiometry problems using partial pressures.

Using Partial Pressures

Dalton's Law tells us that the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases. For each of the gases in the mixture, the partial pressure of a gas in a mixture is directly proportional to the mole fraction of that gas. Given this proportionality, **stoichiometry problems involving gas mixtures may be solved in terms of partial pressures**! The use of partial pressures in a stoichiometry calculation for mixtures of gases is illustrated in the following example.

Example 3.1.7.1: Partial Pressures and Stoichiometry

A sealed, rigid, container holds a 50/50 mixture of nitrogen and hydrogen gas at a total pressure of 1.50 atm. A reaction occurs as follows:

$$\mathbf{N_2 + 3\,H_2 \rightarrow 2\,NH_3} \tag{3.1.7.1}$$

Assuming that the volume and temperature are constant, what is the final total pressure in the container after the reaction has gone to completion?

Given: mixture ratio, total pressure, chemical reaction

Asked for: total pressure after reaction

Strategy:

A. Set up ICE table in terms of partial pressures.
B. Add together the final partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A Set up an ICE table in terms of partial pressures. Note that the initial initial total pressure of 1.50 atm must be half due to nitrogen and half due to hydrogen gas, so each gas is initially present with a partial pressure of 0.75 atm.

	$\mathbf{N_2}$	$\mathbf{3\ H_2}$ -->	$\mathbf{2\ NH_3}$
Initial	0.75 atm	0.75 atm	0 atm

As we consider the chemical change that occurs, we will recognize that the coefficients from the balanced chemical equation may be applied to the partial pressures (since these are proportional to the moles of each gas present.) For example, after determining that hydrogen gas is the limiting reactant, we may calculate the amount of nitrogen gas that will be consumed:

$$0.75\,atm\,H_2 \times \frac{1\,atm\,N_2}{3\,atm\,H_2} = 0.25\,atm\,N_2 \tag{3.1.7.2}$$

Using these ideas, we can complete the "change" row of the ICE table:

	N_2	3 H_2 -->	2 NH_3
Initial	0.75 atm	0.75 atm	0 atm
Change	-0.25 atm	-0.75 atm	+0.50 arm

Completing the table by summing down the columns, we have the following completed ICE table, in units of atm:

	N_2	3 H_2 -->	2 NH_3
Initial	0.75 atm	0.75 atm	0 atm
Change	-0.25 atm	-0.75 atm	+0.50 atm
End	0.50 atm	0 atm	0.50 atm

At the end of this reaction, the container would hold a mixture of N_2 (the excess reactant) and NH_3 (the product).

B We can now sum the end partial pressures to calculate the total pressure in the container:

$$P_{tot} = P_{N_2} + P_{NH_3} = 0.50\,\text{atm}\,N_2 + 0.50\,\text{atm}\,NH_3 = 1.00\,\text{atm total} \quad (3.1.7.3)$$

Exercise 3.1.7.1

Samples of oxygen gas and xenon gas are added to an evacuated container of fixed volume and the following reaction occurs forming a yellow solid:

$$Xe(g) + 2\,O_2(g) \rightarrow XeO_4(s)$$

The initial partial pressure of the oxygen gas is 2.0 atm and that of the xenon gas is 0.7 atm. After the reaction has gone to completion, what is the total pressure inside the container? The temperature remained constant. Note: the solid product will NOT contribute to the gas pressure.

Answer

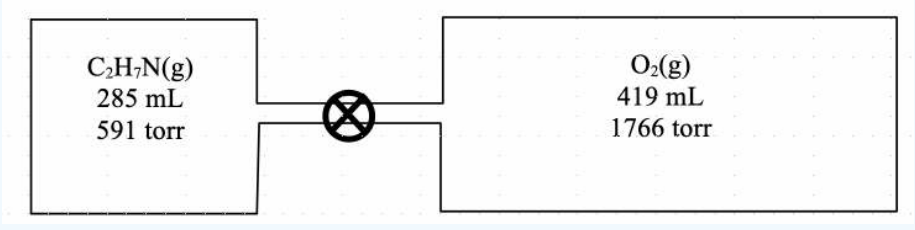
P_{total} = 0.6 atm (note, in this case, the total pressure is simply the pressure of the excess reactant)

Warning: Not All Pressures Are Partial Pressures!

Remember, partial pressures are used to describe a **mixture** of gases. The above example problem began with gases in a single container, all mixed together. However, many problems you encounter may start with the gases separated. Consider the situation illustrated in Example \(\PageIndex{2}\).

Example 3.1.7.2: Bulbs Separated by Valves

Consider the apparatus pictured below, which consists of two containers separated by a valve.



The valve is opened and the gases react as follows (note that the temperature is high enough that the water is produced as a gas):

$$4\,C_2H_7N(g) + 15\,O_2(g) \rightarrow 8\,CO_2(g) + 14\,H_2O(g) + 2\,N_2(g)$$

What will be the total pressure in the apparatus when the reaction has gone to completion? Assume that the temperature does not change.

Given: pressure and volume of each gas prior to the valve being open, chemical equation

Asked for: the total pressure in the apparatus when the reaction has gone to completion

Strategy: In this problem, we must consider two processes: each gas expands to fill the entire system, and the gases react with one another. These two processes actually occur at the same time, but we must treat them as if the expansion occurs first.

Solution:

First we will calculate the pressure that each gas exerts after expanding to fill the container:

The C_2H_7N expands from 285 mL to 704 mL (285 mL + 419 mL):

$$591 \text{ torr} \times 285 \text{ mL} = P_2 \times 704 \text{ mL}$$

$$P_2 = 239.25 \text{ torr}$$

The O_2 expands from 419 mL to 704 mL:

$$1766 \text{ torr} \times 419 \text{ mL} = P_2 \times 704 \text{ mL}$$

$$P_2 = 1051.07 \text{ torr}$$

Now, we consider the reaction. Since the volume of the entire system and the temperature are constant, we can do our stoichiometry using partial pressures. (Note that we can not use the pressures given in the problem to do stoichiometry!) Here is an ICE table for the reaction. Note that C_2H_7N is the limiting reactant here.)

	$4\ C_2H_7N$	$+\ 15\ O_2$	$\rightarrow 8\ CO_2$	$+\ 14\ H_2O$	$+\ 2\ N_2$
Initial	239.25 torr	1051.07 torr	0 torr	0 torr	0 torr
Change	–239.25 torr	–897.19 torr	+478.50 torr	+837.38 torr	+119.63 torr
End	0 torr	153.88 torr	478.50 torr	837.38 torr	119.63 torr

Finally, we calculate the total pressure in the system after the reaction:

153.88 torr + 478.50 torr + 837.38 torr + 199.63 torr = **1590 torr** (rounded from 1589 torr)

Summary

The partial pressure of each gas in a mixture is proportional to its mole fraction. Partial pressures may be used in solving stoichiometry problems.

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3.1.8: Kinetic-Molecular Theory

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:

five postulates of Kinetic Molecular Theory

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.

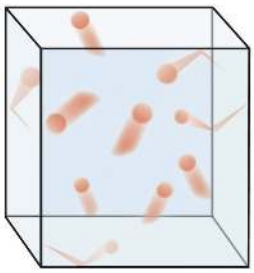


Figure **3.1.8.1:** *Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.*

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 3.1.8.2).

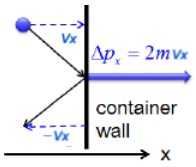


Figure **3.1.8.2**: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. v_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the 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 v_x in x direction hits is expressed as:

$$\Delta p_x = 2mv_x \tag{3.1.8.1}$$

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.

$$f \propto (v_x) \times \left(\frac{N}{V}\right) \tag{3.1.8.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mv_x) \times (v_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mv_x^2 \tag{3.1.8.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace v_x^2 in the expression above with the average value of v_x^2, which is denoted by $\overline{v_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{v_x^2} \tag{3.1.8.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}. \tag{3.1.8.5}$$

Here the quantity $\overline{v^2}$ is called the **mean-square speed** defined as the average value of square-speed (v^2) over all molecules. Since

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{3.1.8.6}$$

for each molecule, then

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}. \tag{3.1.8.7}$$

By substituting $\frac{1}{3}\overline{v^2}$ for $\overline{v_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{v^2} \tag{3.1.8.8}$$

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, which can be represented ($\overline{KE}_{mc}$):

$$\overline{KE}_{mc} = \frac{1}{2} m\overline{v^2} = \frac{3}{2}\frac{R}{N_A} T \tag{3.1.8.9}$$

where N_A is the Avogadro's constant. In Chemistry 101A, we will most commonly discuss the average translational kinetic energy of 1 mole of molecules. This can be obtained by multiplying the above equation by N_A:

$$N_A\overline{KE}_{mc} = N_A\frac{1}{2}m\overline{v^2} = \frac{3}{2}RT$$

where N_Am equals the molar mass of the gas M in kg/mol. Thus, the average translational kinetic energy, ($\overline{KE}$), of the gas (in units of J/mol) can be expressed as:

$$\overline{KE} = \frac{3}{2}RT \tag{3.1.8.10}$$

By rearranging the equation, we can get the relationship between the root-mean square speed (v_{rms}) and the temperature. The rms speed (v_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{v_1^2 + v_2^2 + \cdots v_N^2}{N}} \tag{3.1.8.11}$$

where N is the number of particles and v_i is the speed of particle i.

The relationship between v_{rms} and the temperature is given by:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{3.1.8.12}$$

In Equation 3.1.8.12, v_{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). Equation 3.1.8.12 shows that v_{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_{mp}) 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 3.1.8.11 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_{mp} increases.

Example 3.1.8.1

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_{ave}) root mean square speed (v_{rms}), and most probable speed (v_{mp}).

Given: particle speeds

Asked for: average speed (v_{ave}), root mean square speed (v_{rms}), and most probable speed (v_{mp})

Strategy:

Use Equation ??? to calculate the average speed and Equation 3.1.8.11 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:

$$v_{\text{ave}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \mathrm{m^2/s^2}}{8}} = 6.2\ \mathrm{m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_{mp} = 6.0$ m/s. The u_{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. 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 **3.1.8.3**. 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 **3.1.8.3** 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.

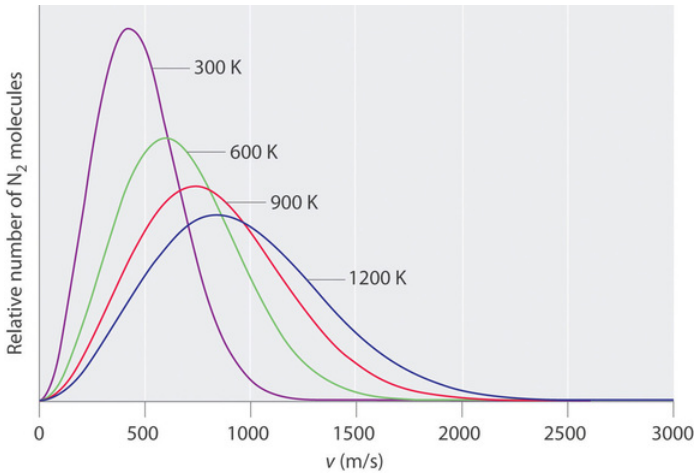


Figure **3.1.8.3** The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

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 3.1.8.2

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

a. average kinetic energy of the N_2 molecules?
b. rms speed of the N_2 molecules?
c. average speed of the N_2 molecules?
d. impact of each N_2 molecule on the wall of the container during a collision with the wall?
e. total number of collisions per second of N_2 molecules with the walls of the entire container?
f. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
g. 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:

a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
c. If the rms speed of the N_2 molecules increases, the average speed also increases.
d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
f. 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.
g. 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 3.1.8.2

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

a. average kinetic energy of the He atoms?
b. rms speed of the He atoms?
c. average speed of the He atoms?
d. impact of each He atom on the wall of the container during a collision with the wall?
e. total number of collisions per second of He atoms with the walls of the entire container?
f. number of collisions per second of He atoms with each square centimeter of the container wall?
g. pressure of the He gas?

Answer a

no change

Answer b

no change

Answer c

no change

Answer d

no change

Answer e

decreases

Answer f

decreases

Answer g

decreases

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:**

$$\overline{KE} = \frac{3}{2}RT$$

- **Root mean square speed:**

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

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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3.1.9: Understanding the Value Distribution of a Variable

Discrete and Continuous Variables

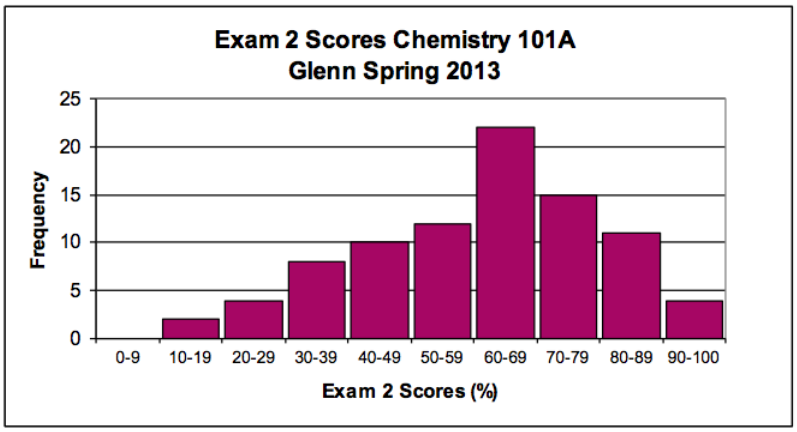
Variables such as *number of children* in a household are called discrete variables since the possible values are discrete points on the scale. For example, a household could have three children or six children, but not 4.53 children. Other variables, such as *percentage of class points earned*, are continuous variables since the scale is continuous and not made up of discrete steps. The percentage could be 82.5%, or it could be 82.5149087%. Of course, the limitations of measurement, or the realities of keeping a grade book, preclude many variables from ever being truly continuous, but when measured with enough precision these variables are considered continuous for practical purposes.

Grouped Frequency Distribution for a Variable

The frequency distribution for a variable consists of possible values for that variable and a count of the number of occurrences of each group of values. Consider the following grouped frequency distribution for a collection of exam scores. Typically, a grouped frequency distribution is portrayed using a histogram.

Grouped Frequency Distribution for a Collection of Exam Scores

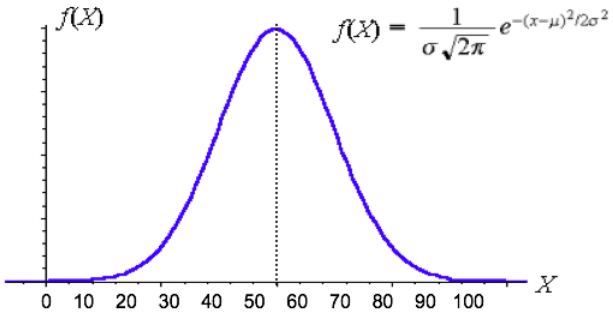
Score	0-9	10-19	20-29	30-39	40-49	50-59	60-69	70-79	80-89	90-100	***(0 -100)***
Frequency	0	2	4	8	10	12	22	15	11	4	***(88)***



Continuous Distribution for a Variable (Probability Density)

The histogram above portrays the actual scores from the 88 students that took this single exam in Spring 2013. However, suppose we plan to give this same exam to thousands of chemistry 101A students all throughout the state and we want to know the ***occurrence probability*** for scores between 60 and 100 percent. (That's just another way to say we want to know what ***fraction of scores*** will be between 60 and 100 percent.) In order to accurately answer this question, we need a reasonable model for the distribution of possible values.

Mathematical equations are often used to define continuous distributions and these models are used to answer exactly this type of question. (Continuous distributions can also be called probability densities.) The normal distribution or "bell curve" is, perhaps, the best known example of a continuous distribution. Many empirical distributions are approximated well by mathematical distributions such as the normal distribution. An example of a normal distribution is shown below. Many exam score distributions are modeled using a similar curve.



The y-axis in the distribution technically represents the “fraction per unit” or the "probability density." You do not use the actual y-axis values very often and no y-values are shown in the image above. Intuitively, the y-axis value tells you the chance of obtaining values *near* corresponding points on the x-axis. In the normal distribution pictured, the probability of an observation with a value *near 40* is about half of the probability of an observation with value *near 50*. The **most probable value** is the value of x corresponding to the highest value of y (the “peak” of the curve.) In the normal distribution pictured, 55 the most probable value of x.

Although we will not discuss the concept of a continuous distribution in great detail, you must be familiar with the following ideas:

1) **The fraction of sample values equal to an exact single value of x is a very small number!** Consider our exam score example. What fraction of exams will have a score equal to *exactly* 82.31 percent? That’s a ridiculously specific score! So, it should make sense that the fraction of exams that have that score is going to be a very, very, very small number. The fraction of exams that will have a score equal to *exactly* 82.31956432342346576 percent is essentially zero. (We can make the fraction as close as we like to zero by making the exam score more and more precise.)

2) **Continuous distributions are best used to determine the fraction of sample with values within a range of x values.** Again, consider the exam score example. What fraction of exams will have a score between 80 and 90 percent? That will be a significant portion of the sample and we would expect that the fraction of exams with scores within that range will be much larger than the fraction for a single score (as described above.)

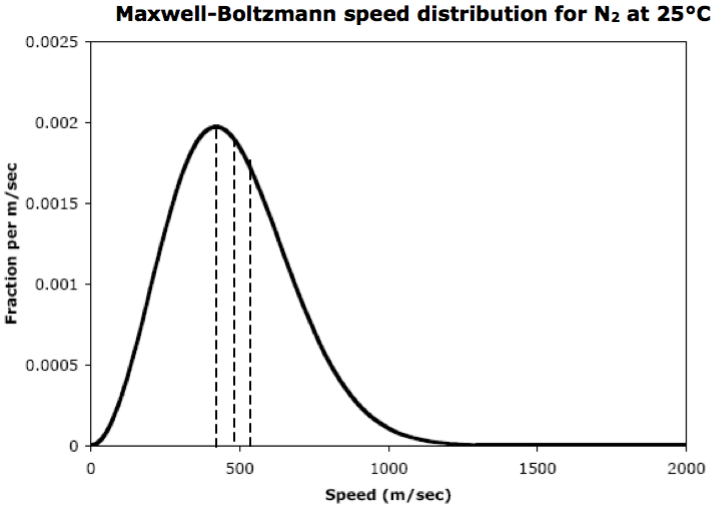
3) **The fraction of area under the curve in any particular region tells you the fraction of the sample with values within that range. For a normalized distribution, the total area under the curve equals 1.** Suppose that one tenth of the exam scores are between 80 and 90 percent. This can be seen in the distribution plot! The continuous distribution for the scores would have a shape that places one tenth of the area below the curve in the region bounded by 80 and 90 on the x-axis.

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3.1.10: Molecular Speed Distribution

Distributions of the Value of Molecular Speed

In the mid-19th century, James Maxwell and Ludwig Boltzmann derived an equation for the distribution of molecular speeds in a gas. Graphing this equation gives us the *Maxwell-Boltzmann distribution of speeds.* The Maxwell-Boltzmann speed distribution curve for N_2 at 25ºC is shown below.



The **x-axis** shows the speeds of the molecules. The overwhelming majority of nitrogen molecules have speeds between 0 and 1000 m/sec at 25ºC.

The **y-axis** shows the fraction of molecules whose speeds lie within ±0.5 m/sec of the speed shown on the x-axis.

For example, when the speed is 500 m/sec, the *y* value is 0.00185. This tells us that the fraction of molecules that have speeds near 500 m/sec is 0.00185. Note: if you are struggling with the concept of the fraction, translate it into a percentage (multiply by 100): 0.185% of the molecules have speeds in this range. The higher the curve at a given speed, the more molecules travel at that speed. For example, many molecules have speeds around 500 m/sec, whereas few molecules have speeds around 1000 m/sec.

The speed that corresponds to the peak of the curve is called the **most probable speed**. More molecules travel at (or close to) this speed than any other. For N_2 at 25ºC, the most probable speed is 421 m/sec. The **average speed** is a little larger than the most probable speed. For N_2 at 25ºC, the average speed is 475 m/sec. The **root-mean-square speed** is the speed that corresponds to the average kinetic energy of the molecules. For N_2 at 25ºC, the root-mean-square speed is 515 m/sec.

For any gas, these speeds can be calculated by the following formulas:

most probable speed:

$$v_{mp} = \sqrt{\frac{2RT}{M}}, \tag{3.1.10.1}$$

average speed:

$$v_{ave} = \sqrt{\frac{8RT}{\pi M}}, \tag{3.1.10.2}$$

root-mean-square speed:

$$v_{rms} = \sqrt{\frac{3RT}{M}}, \tag{3.1.10.3}$$

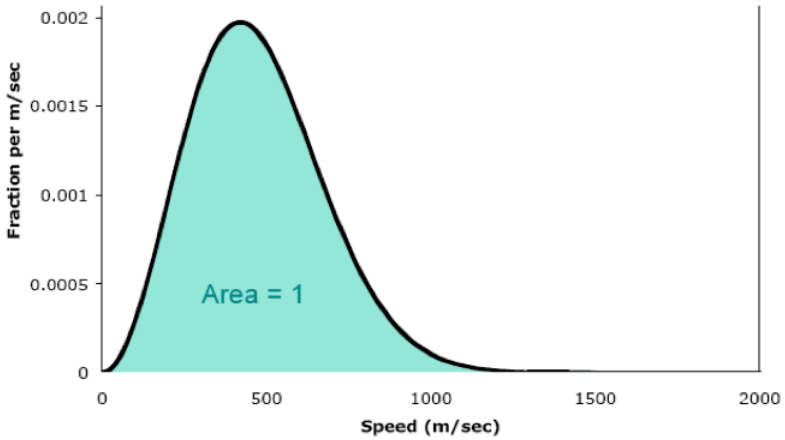
where T is the kelvin temperature, R is the gas constant expressed in units of J/mol-K (8.314 J/mol-K), and M is the molar mass of the gas expressed in units of kg/mol.

Fraction of Molecules in a Wide Range of Speeds

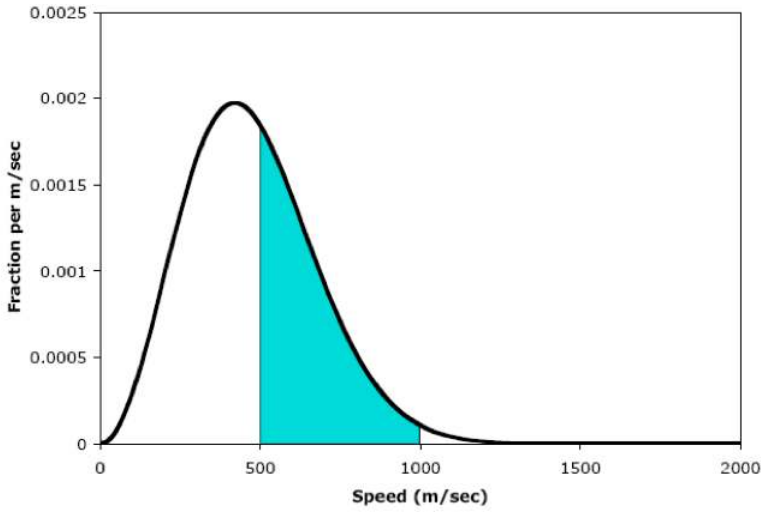
Suppose we wanted to know the fraction of molecules that have speeds in a wide range, say 500 to 1000 m/sec. In principle, we could add up the fractions for each individual speed in this range, just as we added up the sizes of the bars in our histogram.

However, in practice this is not practical, because there would be way too many “bars” to add up (for this particular range we’d need to add up 500 “bars”!!) A far better way to determine the fraction of molecules in a wide range of speeds is to measure the area of the region under the Maxwell-Boltzmann curve.

The area under the entire Maxwell-Boltzmann curve is exactly 1. Therefore, the area under any part of the curve equals the fraction of molecules in the corresponding velocity range.



For example, if we want to determine the fraction of molecules that have velocities between 500 and 1000 m/sec, we need to measure the area of the shaded region below.



There are several ways to estimate this area. The simplest, which you will do in the lab, is to cut out and weigh the graph. In principle, we could use calculus to determine the exact area under the curve, since the equation that generates the Maxwell-Boltzmann curve is known. Unfortunately, this equation cannot be integrated analytically. If you’re curious, though, the area of the shaded region is 0.392, so the fraction of molecules that have speeds between 500 and 1000 m/sec is 0.392. (As always, we can think of this as a percentage: 39.2%.)

The Shape of a Speed Distribution Curve

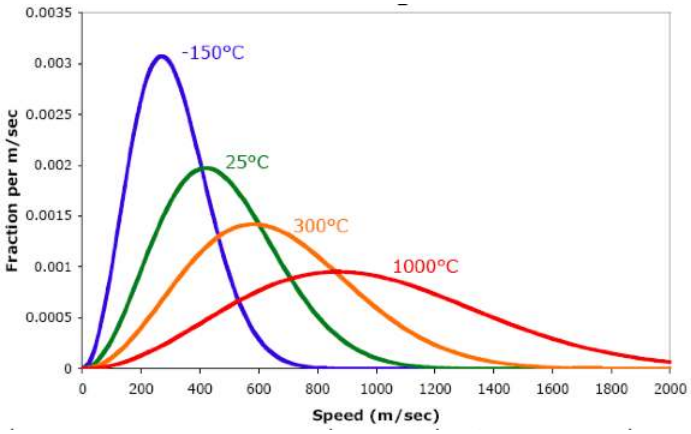
A great deal of information about a gas can be gleaned by considering the overall shape of the speed distribution curve. The speed distribution curve shape will vary with both temperature and molar mass of the gas.

Speed Distributions at Different Temperatures

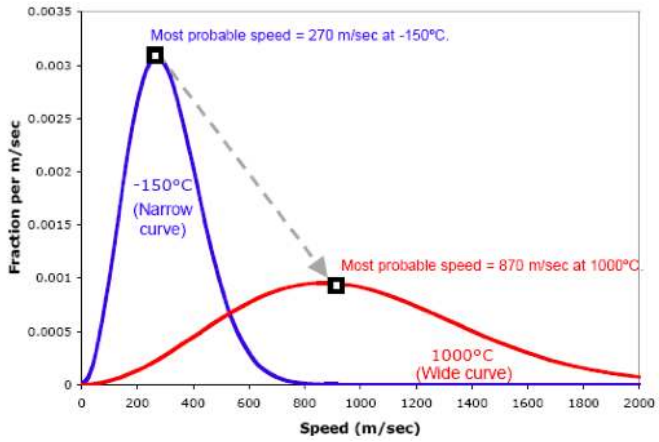
When we consider a gas at increasing temperature:

- The Maxwell-Boltzmann curve spreads and flattens out.
- The most probable speed increases (the peak shifts to the right).
- The fraction of fast-moving molecules increases.
- The fraction of slow-moving molecules decreases.

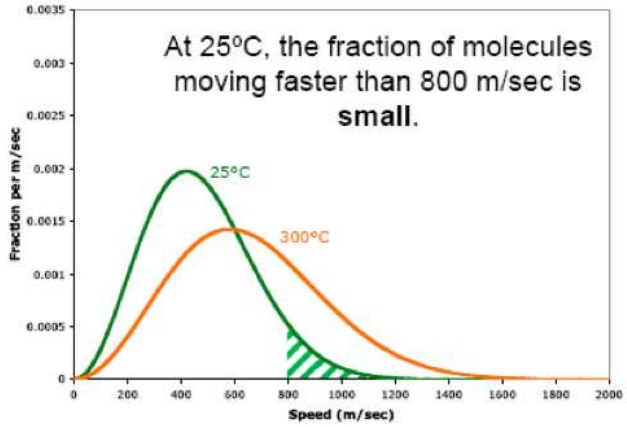
Consider the following distributions showing nitrogen gas at four different temperatures.

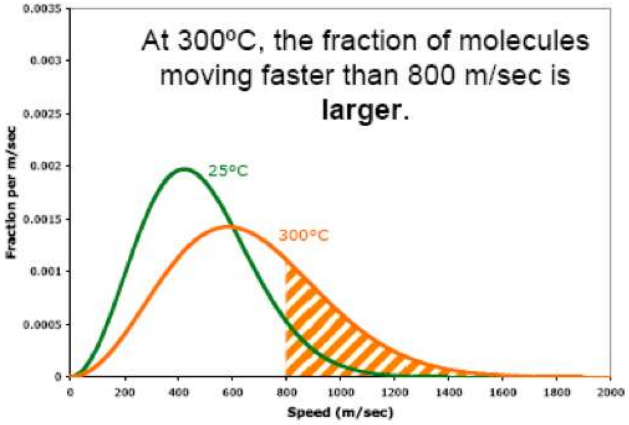


Observe that when the temperature goes up, the particles in a gas tend to move faster. As a result, the entire distribution shifts to the right, toward higher speeds. When we raise the temperature, the most probable speed increases (the highest point on the curve shifts to the right). In addition, the entire curve gets wider and lower: we have a wider range of speeds, but we have fewer molecules at the most probable speed.

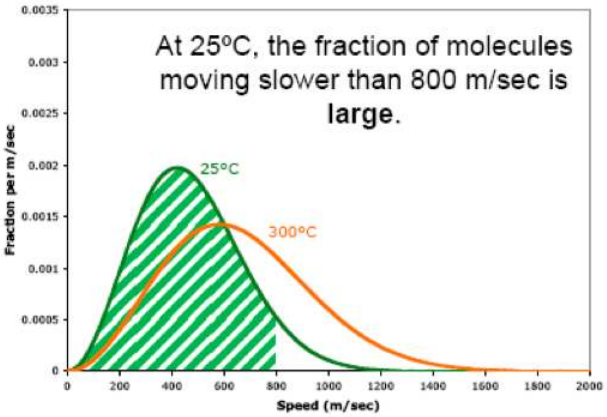


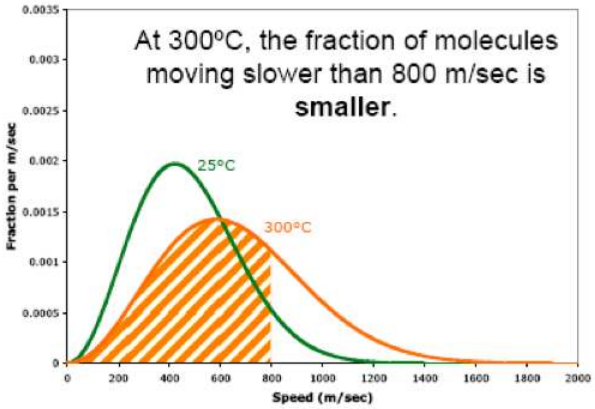
Also, when we raise the temperature, the fraction of molecules moving at **high** speeds **increases**. For example, when we raise the temperature from 25ºC to 300ºC, the fraction of molecules moving faster than 800 m/sec becomes larger.





Likewise, when we raise the temperature, the fraction of molecules moving at **low** speeds **decreases**. For example, when we raise the temperature from 25ºC to 300ºC, the fraction of molecules moving slower than 800 m/sec becomes smaller.



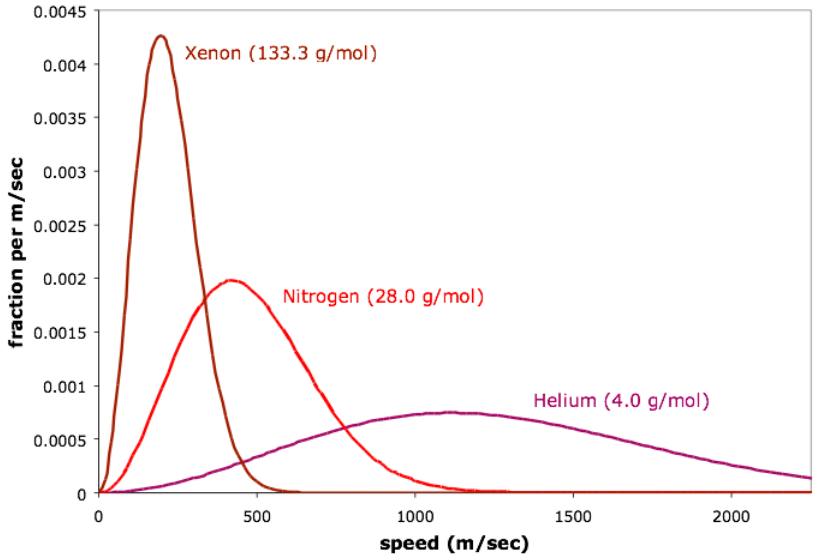


Speed Distribution Curves for Different Molar Masses

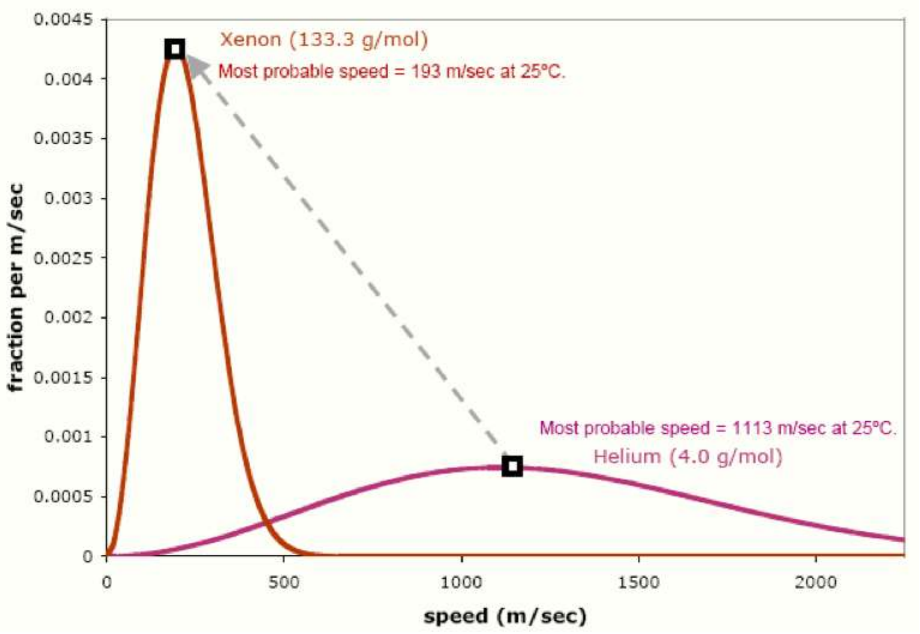
When we consider gases of increasing molar mass:

- The Maxwell-Boltzmann curve gets taller and narrower.
- The most probable speed decreases (the peak shifts left).
- The fraction of fast-moving molecules decreases.
- The fraction of slow-moving molecules increases.

Consider the following Maxwell-Boltzmann speed distribution curves for three different gases.



Observe that the gas with the lowest molar mass (helium) has the highest molecular speeds, while the gas with the highest molar mass (xenon) has the lowest molecular speeds. When we increase the molar mass, the most probable speed decreases (the highest point on the curve shifts to the left). In addition, the entire curve gets narrower and taller: we have a smaller range of speeds, but we have more molecules at the most probable speed.



Example 3.1.10.1: Which is larger?

For each of the following pairs of quantities, tell which one is larger and explain your answer. If they are equal, say so and explain how you can tell. ("KE" means kinetic energy)

a) The rms velocity of nitrogen at 25ºC or the rms velocity of oxygen at 75ºC.

b) The average velocity of hydrogen or the average velocity of helium at the same temperature.

c) The fraction of CH_4 molecules with velocities greater than 500 m/sec, or the fraction of NH_3 molecules with velocities greater than 500 m/sec at the same temperature.

Solutions:

a) **Oxygen at 75ºC** is larger. The rms velocity depends on both the molar mass and the temperature, so it is easiest to just calculate the rms velocity for each gas, v_{rms} for N_2 is 515 m/s and for O_2 is 521 m/s.

b) **Hydrogen** is larger. If the temperature is constant, the velocity distribution is inversely dependent on the molar mass; the smaller the molar mass, the faster the molecules.

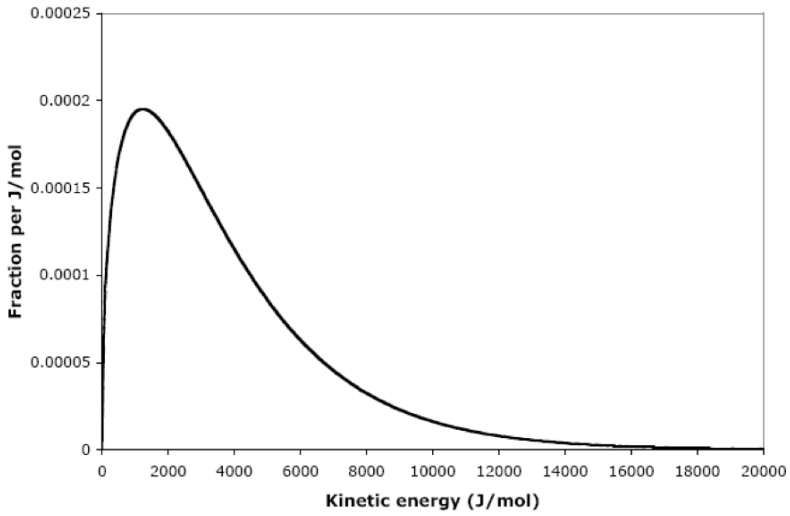
c) The fraction of **CH_4 molecules** with velocities greater than 500 m/sec is larger. This is similar to part c. The gas with the smaller molar mass will have a larger fraction of “fast molecules” and a smaller fraction of “slow molecules”, no matter where we choose the cutoff between “fast” and “slow”.

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3.1.11: Kinetic Energy Distribution

Distributions of the Value of Molecular Kinetic Energy

The Maxwell-Boltzmann equation can also be expressed in terms of the distribution of molecular kinetic energies in a gas. Graphing this equation gives us the *Maxwell-Boltzmann distribution of kinetic energies*. The Maxwell-Boltzmann kinetic energy distribution curve for N_2 at 25ºC is shown below.

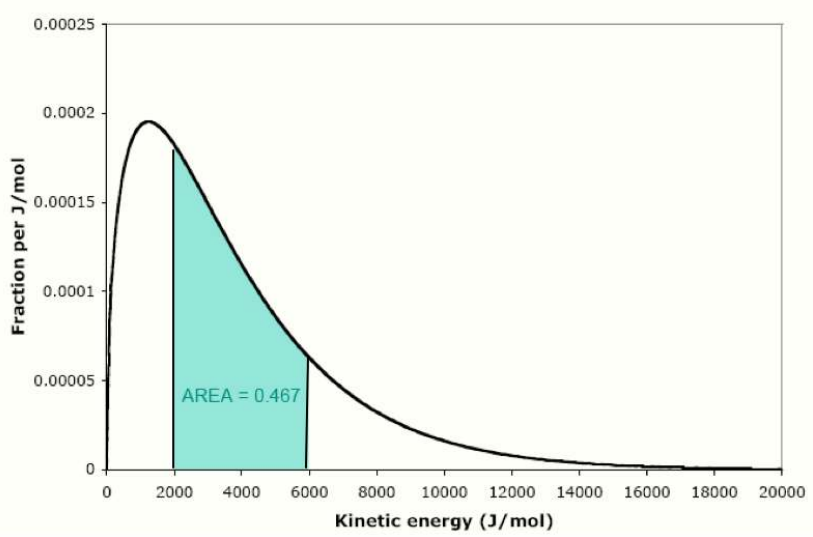


The *x*-axis shows molecular kinetic energies in units of joules per mole. Expressing particle energies in joules per mole is analogous to expressing atomic weights in grams per mole. If we wish to calculate the energy of a single particle, we simply divide the value in J/mol by Avogadro's number.

The *y*-axis shows the fraction of particles whose energies are *near* the corresponding value on the *x*-axis.

For instance, the fraction of molecules that have kinetic energies *near* 4000. J/mol (the range 4000 ± 0.5 J/mol) is 0.000115. Another way to say the same thing is: "0.0115% of the nitrogen molecules have kinetic energies near 4000. J/mol."

We can measure the fraction of molecules having a wide range of energies by measuring the area under the curve. For instance, the fraction of area of the shaded region is 0.467, so the fraction of nitrogen molecules that have energies between 2000 and 6000 J/mol is 0.467 (that's 46.7%). Recall that the total area under this curve is exactly 1.



The kinetic energy corresponding to the peak of the curve is called the **most probable kinetic energy.** The **average kinetic energy** is much larger than the most probable kinetic energy. For any gas, these kinetic energy values can be calculated by the following formulas:

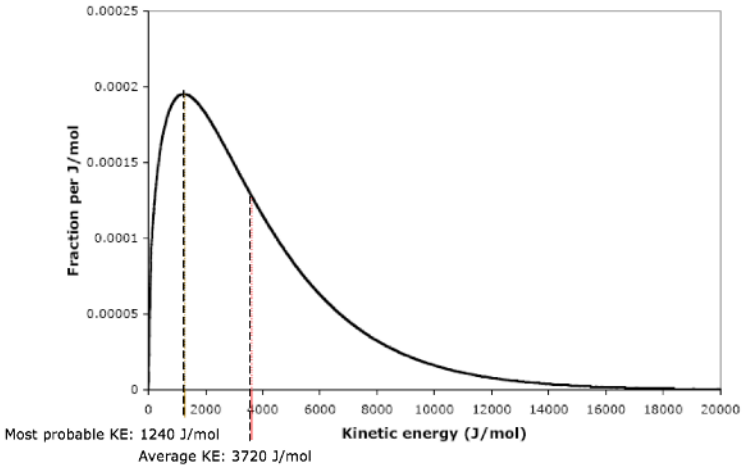
most probable kinetic energy, KE_{mp}:

$$KE_{mp} = \frac{1}{2}RT \tag{3.1.11.1}$$

average kinetic energy, KE_{ave}:

$$KE_{ave} = \frac{3}{2}RT \tag{3.1.11.2}$$

where T is the kelvin temperature, R is the gas constant expressed in units of J/mol-K (8.314 J/mol-K). For N_2 at 25ºC, the most probable KE is 1240 J/mol and the average KE is 3720 J/mol.



Note that the average kinetic energy is much larger than the most probable kinetic energy.

Compare this with the speed distribution, where the most probable speed is fairly close to the average speed.

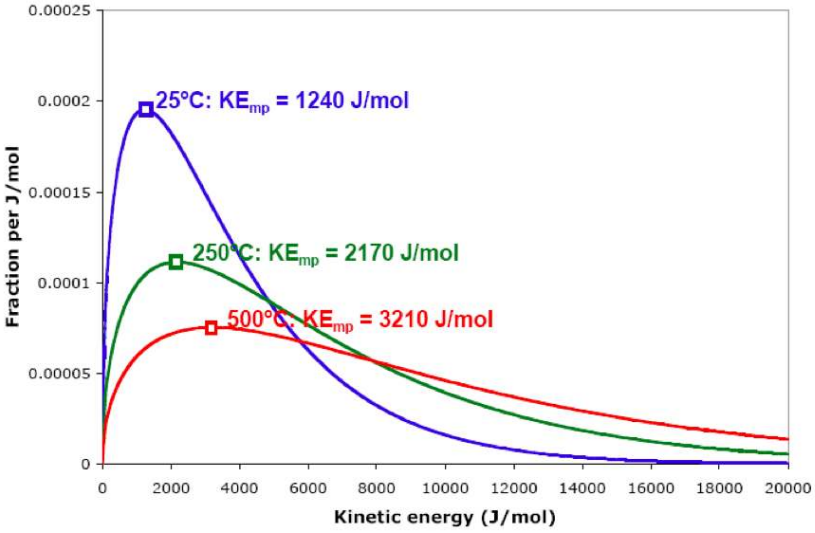
The Shape of a Kinetic Energy Distribution Curve

The kinetic energy distribution curve shape will vary with temperature only. The shape of the kinetic energy distribution is independent of the molar mass of the gas.

When we consider a gas at increasing temperature:

- The Kinetic Energy distribution curve spreads and flattens out.
- The most probable kinetic energy increases (the peak shifts to the right).
- The fraction of higher-energy molecules increases.
- The fraction of lower-energy molecules decreases.

Consider the following graphs for nitrogen gas at 25ºC, 250ºC, and 500ºC. Increasing the temperature increases the most probable KE, and it shifts the entire graph toward higher kinetic energies. Note the change in shape of the distribution. Notice that at higher temperatures, the fraction of molecules with kinetic energies higher than a particular value, such as 4000 J/mol, increases significantly.



Note that the kinetic energy distribution is the same for any gas, as long as the gases are at the same temperature. The mass of the individual particles has no effect on the shape of kinetic energy distribution. The graph shown for N_2 at 25ºC can represent the kinetic energy distribution of H_2, He, O_2, CO_2, Ar, Xe, or any other substance that is a gas at 25ºC.

When we consider different gases at the same temperature:

- The Kinetic Energy distribution curves are identical.
- The shape of a kinetic energy distribution curve is independent of molar mass.

Example 3.1.11.1: Which is larger?

For each of the following pairs of quantities, tell which one is larger and explain your answer. If they are equal, say so and explain how you can tell. (“KE” means kinetic energy)

a) The most probable KE for argon at 25ºC or the most probable KE for neon at 25ºC.

b) The fraction of He atoms with kinetic energies between 100 and 200 J/mol, or the fraction of Ne atoms with kinetic energies between 100 and 200 J/mol, if both gases are at 100ºC.

Solutions:

a) **They have the same most probable kinetic energies.** The kinetic energy distribution depends only on temperature.

b) **Exactly the same fraction of atoms** with kinetic energies in any range we select.To work this out, we must recognize that the kinetic energy distribution depends only on temperature, not on molar mass. Therefore, the helium and the neon will have exactly the same fraction of atoms with kinetic energies in any range we select.

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3.1.12: Molecular Effusion and Diffusion

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.

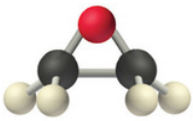
Diffusion and Effusion

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*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{3.1.12.1}$$



Ethylene oxide

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure **3.1.12.1** 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.

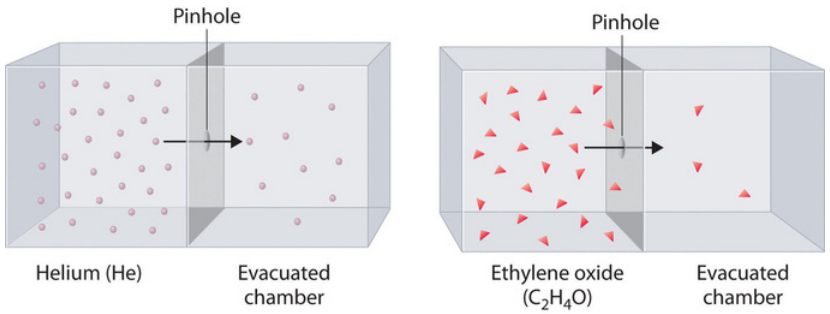


Figure **3.1.12.1**: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 3.1.12.1

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 $^{235}\mathbf{U}$. Naturally occurring uranium is only 0.720% $^{235}\mathbf{U}$, whereas most of the rest (99.275%) is $^{238}\mathbf{U}$, 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 $\boldsymbol{UF_6}$ (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:

A The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is

$$234.04 + (6)(18.998) = 349.03 \text{ g/mol}$$

The molar mass of $^{238}UF_6$ is

$$238.05 + (6)(18.998) = 352.04 \text{ g/mol}$$

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 3.1.12.1:

$$\frac{\text{rate } ^{235}\text{UF}_6}{\text{rate } ^{238}\text{UF}_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \qquad (3.1.12.2)$$

B To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

final purity = (initial purity)(separation)^n

In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$1.0043^n = \frac{0.990}{0.00720} = 137.50 \tag{3.1.12.3}$$

Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{3.1.12.4}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} \tag{3.1.12.5}$$

$$= 1148 \tag{3.1.12.6}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Below is a small part of a system that is used to prepare enriched uranium on a large scale.



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 3.1.12.1

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

Answer 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:

$$KE = \frac{1}{2}\frac{M_A}{N_A}v^2_{rms,A} = \frac{1}{2}\frac{M_B}{N_A}v^2_{rms,B} \tag{3.1.12.7}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v^2_{rms,B}}{v^2_{rms,A}} = \frac{M_A}{M_B} \tag{3.1.12.8}$$

Taking the square root of both sides gives

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{3.1.12.9}$$

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 3.1.12.9 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 **3.1.12.3** 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.

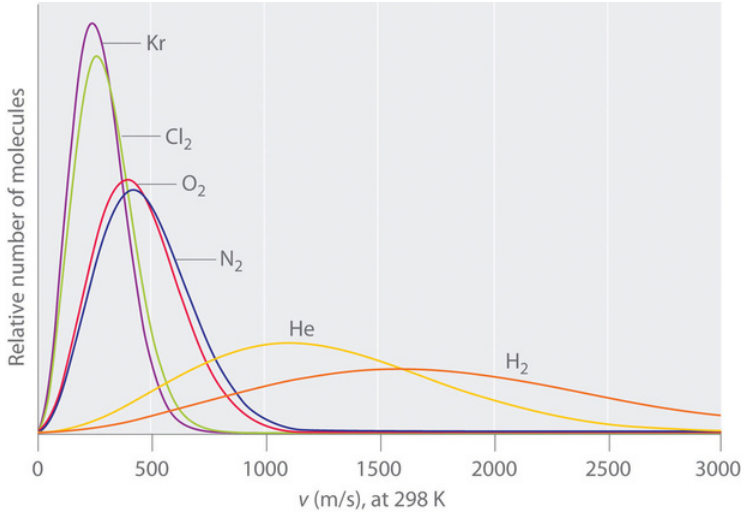


Figure **3.1.12.3**: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

> 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 **3.1.12.4**.

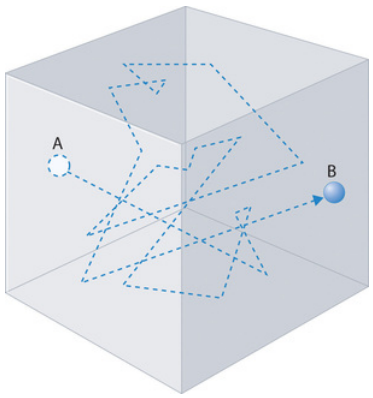


Figure **3.1.12.4**: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

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).

> The **denser** the gas, the **shorter** the mean free path.

Example 3.1.12.2

Calculate the rms speed of a sample -butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of cis-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 10.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 10.8.4, 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

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{3.1.12.10}$$

$$= \sqrt{\frac{3 \times 8.3145 \ \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} \tag{3.1.12.11}$$

$$= 361 \ m/s \tag{3.1.12.12}$$

or approximately 810 mi/h.

Exercise 3.1.12.1

Calculate the rms speed of a sample of radon gas at 23°C.

Answer

$1.82 \times 10^2 \ m/s$ (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not “ideal,” although their behavior usually approximates that of an ideal gas.

Summary

- **Graham’s law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{3.1.12.13}$$

- **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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3.1.13: Real Gases - Deviations from Ideal Behavior

Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure **3.1.13.1***a*). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure **3.1.13.1***b*).

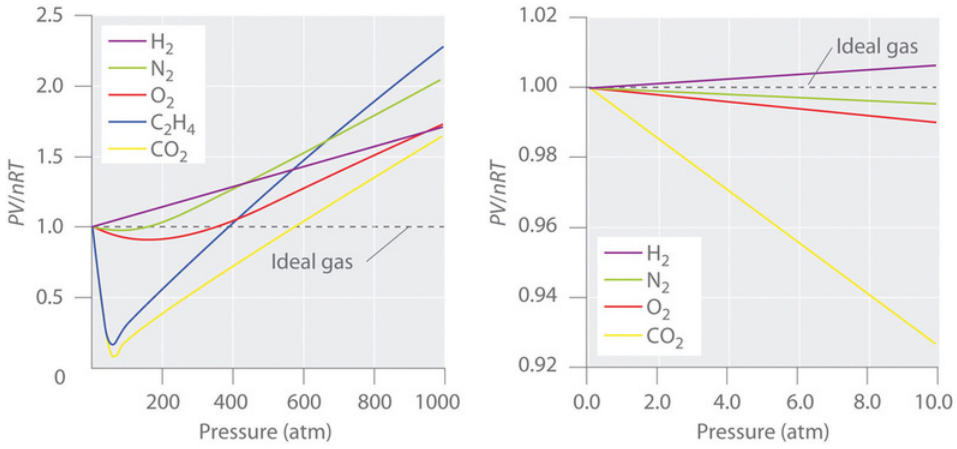


Figure **3.1.13.1**: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of *PV*/*nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure **3.1.13.2** for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

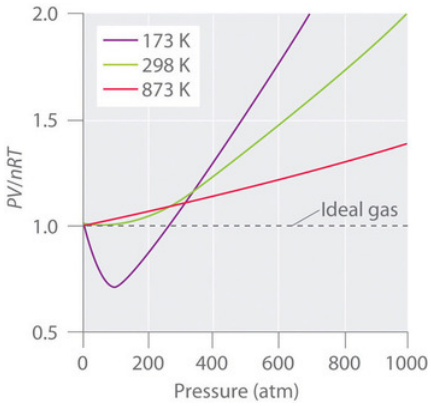


Figure **3.1.13.2**: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure **3.1.13.3**). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.

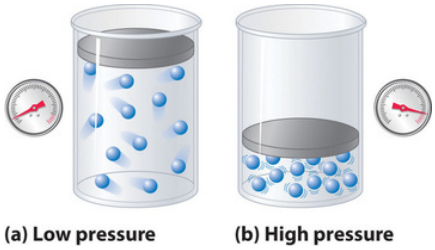


Figure **3.1.13.3**: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure **3.1.13.4**). Thus as shown in Figure **3.1.13.2**, at low temperatures, the ratio of PV/nRT is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas

behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P+\frac{an^2}{V^2}\right)}_{\text{Pressure Term}}\overbrace{(V-nb)}^{\text{Volume Term}}=nRT \tag{3.1.13.1}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table **3.1.13.1** for several common gases.

Table **3.1.13.1**:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a (L^2·atm)/mol^2)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 3.1.13.1 corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure **3.1.13.4**. The volume term corrects for the volume occupied by the gaseous molecules.

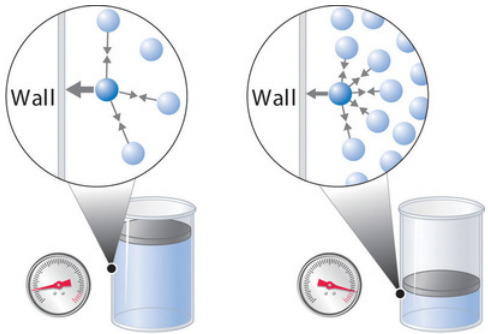


Figure **3.1.13.4**: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on *V* and *P*, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

Example 3.1.13.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table **3.1.13.1**. Use the van der Waals equation (3.1.13.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \tag{3.1.13.2}$$

$$= \frac{500\ \text{g}}{70.906\ \text{g/mol}} \tag{3.1.13.3}$$

$$= 7.052\ mol$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \tag{3.1.13.4}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} \tag{3.1.13.5}$$

$$= 43.1\ atm \tag{3.1.13.6}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table **3.1.13.1**. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{3.1.13.7}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \tag{3.1.13.8}$$

$$= 28.2\ \text{atm} \tag{3.1.13.9}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise 3.1.13.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals equation.

Answer a

77 atm

Answer b

67 atm

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large a coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small a coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

> *A large value of a in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.*

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure* 3.1.13.5*: *A Liquid Natural Gas Transport Ship.*

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure **3.1.13.5**). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of PV/nRT versus P at a given temperature; for an ideal gas, PV/nRT versus P = 1 under all conditions. At high pressures, most real gases exhibit larger PV/nRT values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit PV/nRT values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

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SECTION OVERVIEW

Topic D- Thermochemistry

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

1. Know the meaning of heat and work, and their relationship to energy (the First Law of Thermodynamics).
2. Relate temperature changes and changes of state to the corresponding amounts of heat, using specific heats, heats of fusion, and heats of vaporization.
3. Use standard calorimetric data (temperatures, masses, and specific heats) to calculate ΔE and ΔH for a reaction.
4. Interconvert ΔE and ΔH for a reaction, and calculate the pressure-volume work that occurs under constant-pressure conditions.
5. Calculate the heat produced by a reaction under constant-pressure or constant-volume conditions, given the masses of reactants and either ΔE or ΔH for the reaction.
6. Understand the meaning of enthalpy of formation (ΔH_f) and use enthalpies of formation to calculate ΔH for a reaction.
7. Use Hess's Law to calculate ΔH for a reaction, given appropriate ΔH values for other reactions.
8. Understand the relationship between changes in chemical potential energy and the energy of a reaction.

4.1: Thermochemistry

4.1.1: Energy, Heat and Work
4.1.2: Calorimetry
4.1.3: The First Law of Thermodynamics
4.1.4: Energy and Chemical Change
4.1.5: Enthalpy – A Modified Energy of Reaction
4.1.6: Putting it All Together
4.1.7: Tabulated Enthalpy Values
4.1.8: Hess's Law

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CHAPTER OVERVIEW

4.1: Thermochemistry

Topic hierarchy

4.1.1: Energy, Heat and Work
4.1.2: Calorimetry
4.1.3: The First Law of Thermodynamics
4.1.4: Energy and Chemical Change
4.1.5: Enthalpy – A Modified Energy of Reaction
4.1.6: Putting it All Together
4.1.7: Tabulated Enthalpy Values
4.1.8: Hess's Law

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4.1.1: Energy, Heat and Work

Energy, Heat and Work

Energy is the ability to move an object against a resisting force. Moving an object against a resisting force is called **work**, so we can write our energy definition more formally:

> ***Energy*** *is the ability to do work.*

Work is a way to *transfer* energy from one collection of matter to another. For example, if you lift a backpack, you transfer some of your body's energy to the backpack. You have less energy after you lift the backpack (you can't keep lifting the backpack forever), but the backpack has more energy after it is lifted.

Energy can be used to do work, but it can also do things that do not involve motion and resistance. For example, think about a mixture of gasoline and oxygen. This mixture can do a great deal of work if we put it into an engine and then ignite it; that is what happens in an automobile engine. However, we can also simply ignite the mixture in an open beaker; no useful work is done in this case, but the beaker and everything else nearby will become very hot. In this case, the energy has been transferred in the form of **heat**. We now have two ways to transfer energy: heat and work. Here are formal definitions of these two terms:

> ***Work*** *occurs when energy is used to move an object against a resisting force.*
>
> ***Heat*** *occurs when energy is used in any other way.*

It's worth pointing out that the words "work" and "heat" have somewhat different meanings in science than they do in everyday life. In everyday life, "work" can mean things like "doing your homework," but in science, work requires motion. If you lift a heavy box, you do work, but if you just hold the heavy box over your head, you don't (even though you get tired!). Likewise, in everyday life, when we speak of "heat" we usually mean **thermal energy**, the energy that a hot object possesses in greater quantity than a cool object. In science, "heat" is the transfer of energy from a warmer object to a cooler one. An object cannot contain heat, but it can lose or gain energy in the form of heat.

Units of Energy

In order to measure energy, we need a unit for it. In the metric system, the standard unit of energy is the **joule**. The formal definition of a joule is: *A joule is the amount of energy expended when an object is moved 1 meter against a resisting force of 1 newton.* (You can learn all about the concept of force in a physics class.) As for the joule, here are some statements that may help you visualize this unit. A joule is…

…enough energy to lift a one kilogram object 10.2 centimeters.

…enough energy to heat one milliliter of water from 20ºC to 20.24ºC.

…enough energy to keep a 60 watt light bulb glowing for 0.0167 seconds.

Obviously, a joule is a very small amount of energy, and in fact it is an inconveniently small amount when we describe chemical reactions. Chemists usually report energies for reactions in kilojoules (1 kJ = 1000 J).

Sign Conventions for Heat and Work

Heat and work have signs (positive or negative), and the sign of each depends on whether the system we are considering is gaining or losing energy. In this class, if a process makes the system gain energy, q and/or w are positive; if the process makes the system lose energy, q and/or w are negative. We can put this information into four formal statements:

- If heat flows into a system, q is positive.
- If heat flows out of a system, q is negative
- If the surroundings do work on the system, w is positive.
- If the system does work, w is negative.

Note that chemists use these conventions so the signs of q and w correspond the the *energy changes of the system*. If you were instead focused on the energy transferred in or out of the surroundings, you might opt to use the opposite sign conventions. Indeed, many physics and engineering courses choose different sign conventions!

Heat in Physical Processes

When we add energy to an object in the form of heat, the most common results are:

a) The temperature of the object goes up.

b) The object melts (if it is a solid) or boils (if it is a liquid).

Heat and Change in Temperature

When the temperature of an object changes, the relationship between the temperature change and the heat that the object gained or lost is:

$$q = mc\Delta T \tag{4.1.1.1}$$

Here, q stands for heat (in joules), m is the mass of the object that changes temperature (in grams), c is the **specific heat capacity** (or just "specific heat") of the object, and ΔT is the temperature change (in ºC). The specific heat capacity is essentially a conversion factor that relates energy to temperature changes and masses. Every substance has its own specific heat capacity, which depends on the chemical composition of the substance, the state of the substance, and (to some extent) the temperature of the substance. Here are specific heat capacities for the three states of water and for a few other common substances.

Table **4.1.1.1**: Specific Heat Capacities

Substance	Specific Heat Capacity (J/g^oC)		Substance	Specific Heat Capacity (J/g^oC)
Water at 25ºC	4.180 J/g·ºC		Helium (He) at 25ºC	5.193 J/g·ºC
Water at 0ºC	4.218 J/g·ºC		Alcohol (C_2H_5OH) at 25ºC	2.419 J/g·ºC
Ice at 0ºC	2.050 J/g·ºC		Salt (NaCl) at 25ºC	0.864 J/g·ºC
Steam at 100ºC	2.042 J/g·ºC		Gold (Au) at 25ºC	0.129 J/g·ºC

Note that the specific heat capacity of water doesn't change very much over the range 0ºC to 25ºC, but it changes a great deal when we convert the water into ice or steam. Note also that we see a wide range of specific heats when we look at a variety of chemicals; the specific heat of helium is about 40 times as large as that of gold.

Exercise 4.1.1.1: Calculating Energy Required for a Temperature Change

How much energy is required to increase the temperature of a 15.0 g sample of gold from 20.0^oC to 27.3^oC?

Solution

$$q_{gold} = m_{gold}c_{gold}\Delta T_{gold}$$

$$q_{gold} = (15.0g)(0.129J/g{\cdot}^oC)(27.3^oC - 20^oC)$$

$$q_{gold} = 14.1255J = 14.1J$$

Heat and Change in Physical State

So far, we have discussed heat transfers that cause temperature change. However, in a phase transition, heat transfer does not cause any temperature change.

For an example of phase changes, consider the addition of heat to a sample of ice at $-20°C$ (Figure 4.1.1.4) and atmospheric pressure. The temperature of the ice rises linearly, absorbing heat at a constant rate of until it reaches $0°C$. Once at this temperature, the ice begins to melt and continues until it has all melted, absorbing 333 J/g of heat. The temperature remains constant at $0°C$ during this phase change. Once all the ice has melted, the temperature of the liquid water rises, absorbing heat at a new constant rate. At $100°C$ the water begins to boil. The temperature again remains constant during this phase change while the water absorbs 2256 kJ/kg of heat and turns into steam. When all the liquid has become steam, the temperature rises again, absorbing heat at a constant rate. If we started with steam and cooled it to make it condense into liquid water and freeze into ice, the process would exactly reverse, with the temperature again constant during each phase transition.

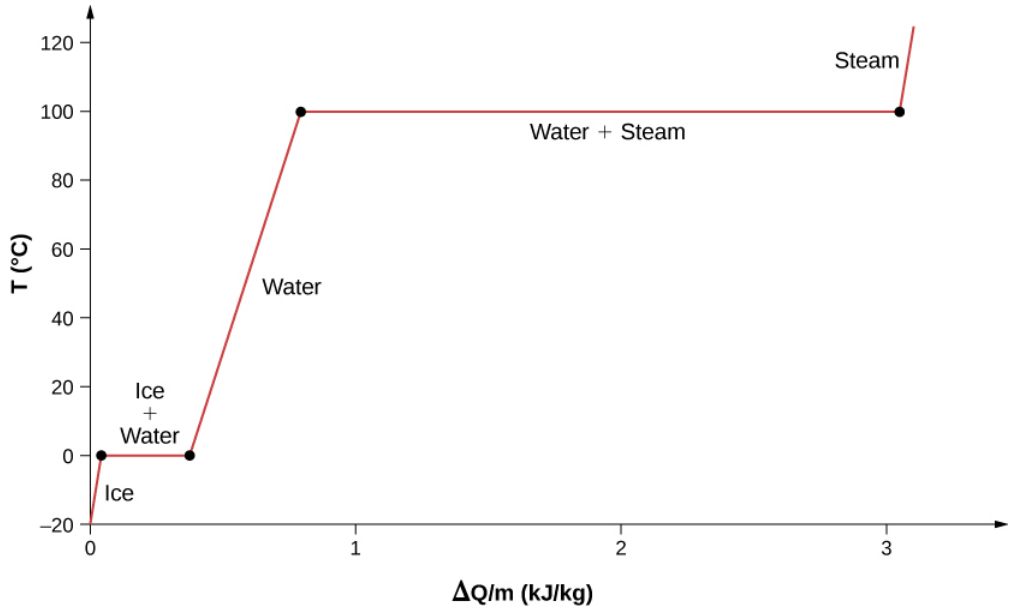


***Figure* 4.1.1.4:** *Temperature versus heat. The system is constructed so that no vapor evaporates while ice warms to become liquid water, and so that, when vaporization occurs, the vapor remains in the system. The long stretches of constant temperatures at $0°C$ and $100°C$ reflect the large amounts of heat needed to cause melting and vaporization, respectively.*

Where does the heat added during melting or boiling go, considering that the temperature does not change until the transition is complete? Energy is required to melt a solid, because the attractive forces between the molecules in the solid must be broken apart, so that in the liquid, the molecules can move around at comparable kinetic energies; thus, there is no rise in temperature. Energy is needed to vaporize a liquid for similar reasons. Conversely, work is done by attractive forces when molecules are brought together during freezing and condensation. That energy must be transferred out of the system, usually in the form of heat, to allow the molecules to stay together (Figure 4.1.1.4). Thus, condensation occurs in association with cold objects—the glass in Figure 4.1.1.5, for example.



***Figure* 4.1.1.5:** *Condensation forms on this glass of iced tea because the temperature of the nearby air is reduced. The air cannot hold as much water as it did at room temperature, so water condenses. Energy is released when the water condenses, speeding the melting of the ice in the glass. (credit: Jenny Downing)*

The energy released when a liquid freezes is used by orange growers when the temperature approaches $0°C$. Growers spray water on the trees so that the water freezes and heat is released to the growing oranges. This prevents the temperature inside the orange from dropping below freezing, which would damage the fruit (Figure 4.1.1.6).



***Figure* 4.1.1.6:** *The ice on these trees released large amounts of energy when it froze, helping to prevent the temperature of the trees from dropping below $0°C$. Water is intentionally sprayed on orchards to help prevent hard frosts. (credit: Hermann Hammer)*

The energy per unit mass required to change a substance from the solid phase to the liquid phase, or released when the substance changes from liquid to solid, is known as the **heat of fusion,** ΔH_{fus}. The energy per unit mass required to change a substance from the liquid phase to the vapor phase is known as the **heat of vaporization** ΔH_{vap}. The strength of the forces depends on the nature of constituent particles of the substance. The heat q required in a phase change in a sample of mass m is given by

$$q = m\Delta H_{fus} \tag{4.1.1.2}$$

$$q = m\Delta H_{vap} \tag{4.1.1.3}$$

where these "heats of transition," ΔH_{fus} and ΔH_{vap} are constants that are determined experimentally. Note that these heats of transformation are also sometimes called "latent heats". These constants are “latent,” or hidden, because during the phase changes, energy enters or leaves a system without causing a temperature change (!) in the system, so in effect, the energy is hidden.

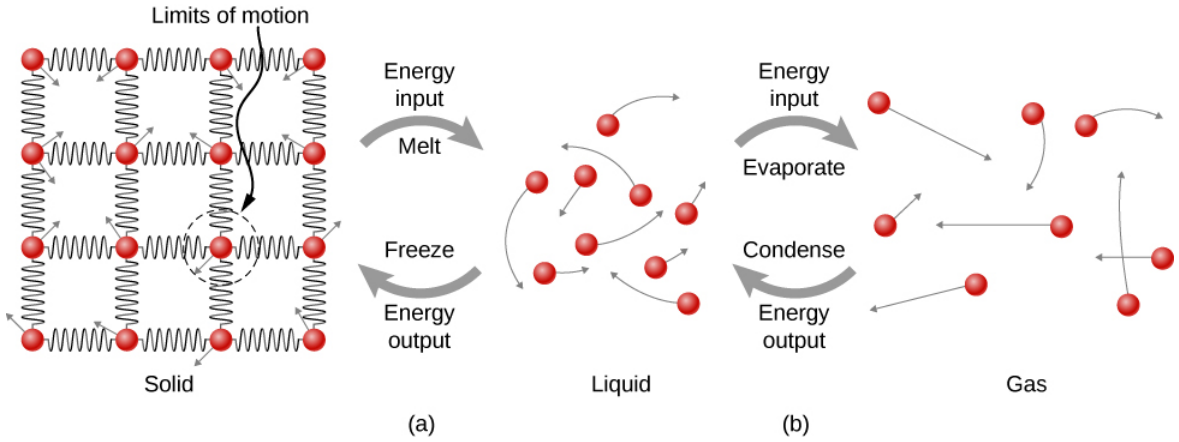


***Figure* 4.1.1.7:** *(a) Energy is required to partially overcome the attractive forces (modeled as springs) between particles in a solid to form a liquid. That same energy must be removed from the liquid for freezing to take place. (b) Particles become separated by large distances when going from liquid to vapor, requiring significant energy to completely overcome molecular attraction. The same energy must be removed from the vapor for condensation to take place.*

Table 4.1.1.2 lists representative values of heats of phase transformation, together with melting and boiling points. Note that in general, $L_v > L_f$. The table shows that the amounts of energy involved in phase changes can easily be comparable to or greater than those involved in temperature changes, as Figure 4.1.1.7 and the accompanying discussion also showed.

Table 4.1.1.2: Heats of Fusion and Vaporization

Substance	Melting Point ($°C$)	ΔH_{fus}, (J/g)	Boiling Point ($°C$)	ΔH_{vap} (J/g)
Mercury	–38.9	11.8	357	272
Water	0.00	334	100.0	2256[3]
Sulfur	119	38.1	444.6	326
Lead	327	24.5	1750	871
Antimony	631	165	1440	561
Aluminum	660	380	2450	11400
Silver	961	88.3	2193	2336
Gold	1063	64.5	2660	1578
Copper	1083	134	2595	5069

Values quoted at the normal melting and boiling temperatures at standard atmospheric pressure ($1\ atm$). [2]Helium has no solid phase at atmospheric pressure. The melting point given is at a pressure of 2.5 MPa. [3]At $37.0°C$ (body temperature), the heat of vaporization for water is 2430 J/g.

Phase changes can have a strong stabilizing effect on temperatures that are not near the melting and boiling points, since evaporation and condensation occur even at temperatures below the boiling point. For example, air temperatures in humid climates rarely go above approximately $38.0°C$ because most heat transfer goes into evaporating water into the air. Similarly, temperatures in humid weather rarely fall below the dew point—the temperature where condensation occurs given the concentration of water vapor in the air—because so much heat is released when water vapor condenses.

More energy is required to evaporate water below the boiling point than at the boiling point, because the kinetic energy of water molecules at temperatures below $100°C$ is less than that at $100°C$, so less energy is available from random thermal motions. For example, at body temperature, evaporation of sweat from the skin requires a heat input of 2428 J/g, which is about 10% higher than the latent heat of vaporization at $100°C$. This heat comes from the skin, and this evaporative cooling effect of sweating helps reduce the body temperature in hot weather. However, high humidity inhibits evaporation, so that body temperature might rise, while unevaporated sweat might be left on your brow.

Note that heats of transformation can be expressed either in joules per gram or in joules per mole. For water, the heat of fusion is 3343.54 J/g. Since a mole of water equals 18.016 grams, the heat of fusion can also be expressed as 333.54 J/g x 18.016 g/mol = 6009.1 J/mol, or 6.009 kJ/mol.

Exercise 4.1.1.2: Calculating Energy Required for a Phase Change

How much energy is required to melt 35.0 g of ice at 0ºC?

Solution

$$q_{melting} = m\Delta H_{fus}$$

$$q_{melting} = (35.0g)(333.5J/g)$$

$$q_{melting} = 1.17x10^4 J = 11.7kJ$$

Like solid-liquid and and liquid-vapor transitions, direct solid-vapor transitions or sublimations involve heat. The energy transferred is given by the equation \(q = m\Delta H_{sub}\), where \(\Delta H_{sub}\) is the **heat of sublimation**, analogous to \

(\Delta H_{fus}\) and \(\Delta H_{vap}\). The heat of sublimation at a given temperature is equal to the heat of fusion plus the heat of vaporization at that temperature.

We can now calculate any number of effects related to temperature and phase change. In each case, it is necessary to identify which temperature and phase changes are taking place. Keep in mind that heat transfer can cause both temperature and phase changes. Here is an example where we are changing both the temperature and the physical state.

Exercise 4.1.1.3: Heat Transfer Involving Both Temperature and Phase Change

Question:

How much heat is required to convert 50.0 g of ice at -10.0ºC into liquid water at 10.0ºC?

Solution:

We must put in enough heat to do three things: raise the temperature of the ice from -10.0ºC to 0ºC, melt the ice, and then raise the temperature of the resulting water from 0ºC to 10.0ºC:

Warming the ice: q_1 = (50.0 g)(2.05 J/g·ºC)[0ºC – (-10.0ºC)] = 1025 J = 1.025 kJ

Melting the ice: q_2 = (50.0 g)(333.5 J/g) = 16675 J = 16.675 kJ

Warming the liquid water: q_3 = (50.0 g)(4.18 J/g·ºC)(10.0ºC – 0ºC) = 2090 J = 2.09 kJ

Total heat required: $q_{total} = q_1 + q_2 + q_3$ = 1.025 kJ + 16.675 kJ + 2.09 kJ = **19.8 kJ**

From the above calculation, we see that a total of 19.8 kJ is required to convert 50.0 g of ice at -10.0ºC into liquid water at 10.0ºC

Exercise 4.1.1.4: Calculating Final Temperature from Phase Change

Question:

Three ice cubes are used to chill a soda at $20°C$ with mass $m_{soda} = 250\,g$. The ice is at $0°C$ and each ice cube has a mass of 6.0 g. Assume that the soda is kept in a foam container so that heat loss can be ignored and that the soda has the same specific heat as water. Find the final temperature when all ice has melted.

Strategy:

The ice cubes are at the melting temperature of $0°C$. Heat is transferred from the soda to the ice for melting. Melting yields water at $0°C$, so more heat is transferred from the soda to this water until the water plus soda system reaches thermal equilibrium. So, in order to solve this problem, we must consider three heat values:

1) Melting the ice at $0°C$:

$$q_1 = m_{ice}\Delta H_{fus}.$$

2) Warming the melted ice to the final equilibrium temperature:

$$q_2 = m_{ice}c_w(T_f - 0°C).$$

3) Cooling the soda to the final equilibrium temperature:

$$q_3 = m_{soda}c_w(T_f - 20°C).$$

Since no heat is lost, only transferred:

$$q_1 + q_2 + q_3 = 0,$$

so that

$$m_{ice}\Delta H_{fus}; + m_{ice}c_w(T_f - 0°C) + m_{soda}c_w(T_f - 20°C) = 0$$

Solve for the unknown quantity

$$T_f = \frac{m_{soda}c_w(20°C) - m_{ice}\Delta H_{fus}}{(m_{soda} + m_{ice})c_w}$$

Solution

First we identify the known quantities. The mass of ice is $m_{ice} = 3 \times 6.0\ g = 18\ g$ and the mass of soda is $m_{soda} = 250\ g$. Then we calculate the final temperature:

$$T_f = \frac{20,930\ J - 6012\ J}{1122\ J/°C} = 13°C$$

Significance This example illustrates the large energies involved during a phase change. The mass of ice is about 7% of the mass of the soda but leads to a noticeable change in the temperature of the soda. Although we assumed that the ice was at the freezing temperature, this is unrealistic for ice straight out of a freezer: The typical temperature is $-6°C$. However, this correction makes no significant change from the result we found. Can you explain why?

Problem-Solving Strategy: The Effects of Heat Transfer

1. Examine the situation to determine that there is a change in the temperature or phase. Is there heat transfer into or out of the system? When it is not obvious whether a phase change occurs or not, you may wish to first solve the problem as if there were no phase changes, and examine the temperature change obtained. If it is sufficient to take you past a boiling or melting point, you should then go back and do the problem in steps—temperature change, phase change, subsequent temperature change, and so on.
2. Identify and list all objects that change temperature or phase.
3. Identify exactly what needs to be determined in the problem (identify the unknowns). A written list is useful.
4. Make a list of what is given or what can be inferred from the problem as stated (identify the knowns). If there is a temperature change, the transferred heat depends on the specific heat of the substance, and if there is a phase change, the transferred heat depends on the heat of transformation of the substance.
5. Solve the appropriate equation for the quantity to be determined (the unknown).
6. Substitute the knowns along with their units into the appropriate equation and obtain numerical solutions complete with units. You may need to do this in steps if there is more than one state to the process, such as a temperature change followed by a phase change. However, in a calorimetry problem, each step corresponds to a term in the single equation $q_{released} + q_{absorbed} = 0$. Note that Exercise 4 is an example of such an equation.
7. Check the answer to see if it is reasonable. Does it make sense? As an example, be certain that any temperature change does not also cause a phase change that you have not taken into account.

Exercise 4.1.1.2

Why does snow often remain even when daytime temperatures are higher than the freezing temperature?

Snow is formed from ice crystals and thus is the solid phase of water. Because enormous heat is necessary for phase changes, it takes a certain amount of time for this heat to be transferred from the air, even if the air is above $0°C$

Practice Problems Involving Heat

1) The specific heat of ethanol (C_2H_5OH) is 2.45 J/g·ºC, and its density is 0.789 g/mL. Using this information, answer the following questions:

a) How much heat is required to raise the temperature of 50.0 mL of ethanol from –5.0ºC to 25.0ºC?

b) If 525 J of heat is added to 25.0 g of ethanol, and the initial temperature of the ethanol is 10.0ºC, what will the final temperature be?

c) A 50.0 g sample of water is placed beside a sample of ethanol whose mass is unknown. The two samples then absorb equal amounts of heat. The temperature of the water increases from 20.0ºC to 28.7ºC, while the temperature of the ethanol increases from 20.0ºC to 31.3ºC. Calculate the mass of the ethanol.

2) Jerry puts a 71.325 g piece of aluminum into a beaker and adds 123.4 g water. How much heat will be required to raise the temperature of the water and the aluminum from 18.4ºC to 31.6ºC? You will need the following information:

Al: specific heat = 0.897 J/g·ºC in this temperature range

H_2O: specific heat = 4.177 J/g·ºC in this temperature range

3) A chemist heats 31.5 g of NaCl crystals to 76.5ºC, and then pours the crystals into 61.2 g of CCl_4. The initial temperature of the CCl_4 is 12.8ºC, and the final temperature is 36.5ºC. The specific heat of CCl_4 (carbon tetrachloride) is 0.751 J/g·ºC. Assuming that no energy is lost to the surroundings, calculate the specific heat of NaCl.

4) You put 12.0 g of ice at 0.0ºC into a coffee-cup calorimeter containing 50.0 g of water at 25.0ºC. Assuming that all the ice melts, determine the final temperature of the cup contents. You'll need the following information for water:

melting point: 0.0 ºC specific heat capacity: 4.18 J/gºC heat of fusion: 333 J/g

5) A chunk of iron at 300.0ºC is added to an insulated container holding 100.0 g of water at 25.0 ºC. What is the minimum mass of iron required to convert all the water into steam at 100.0 ºC?

You'll need the following information:

Water -- boiling point: 100.0 ºC specific heat capacity: 4.18 J/gºC heat of vaporization: 2260 J/g

Iron – specific heat capacity: 0.448 J/gºC

AnswerS to the *Practice Problems Involving Heat*

1) a) 2.90 kJ b) 18.6 °C c) 65.7 g

2) 7.65 x 10^3 J

3) 0.865 J/g°C

4) 4.7 °C

5) 2870 g

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4.1.2: Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure **4.1.2.1**). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

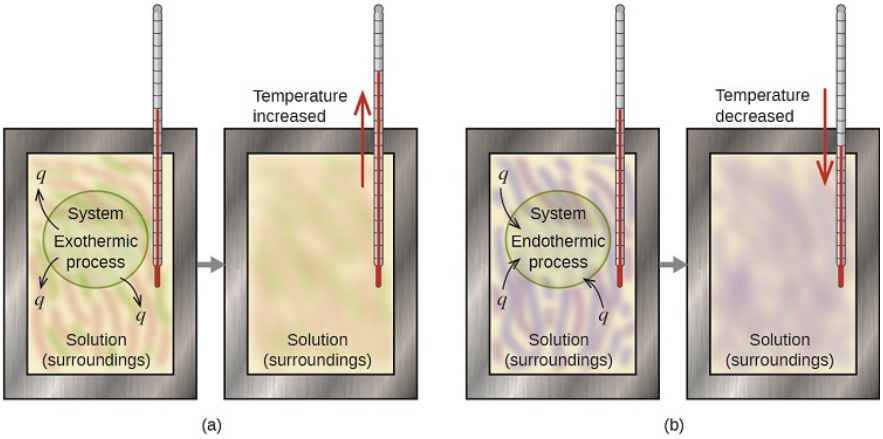


Figure **4.1.2.1**: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

> By convention, q is given a negative (-) sign when the system releases heat to the surroundings (exothermic); q is given a positive (+) sign when the system absorbs heat from the surroundings (endothermic).

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure **4.1.2.2**). These easy-to-use "coffee cup" calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

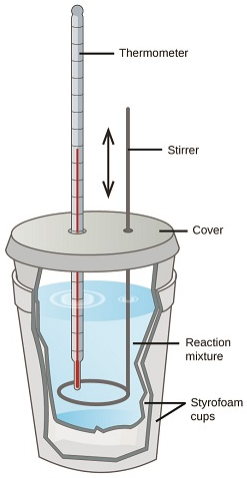


Figure **4.1.2.2**: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive

calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure **4.1.2.3**).

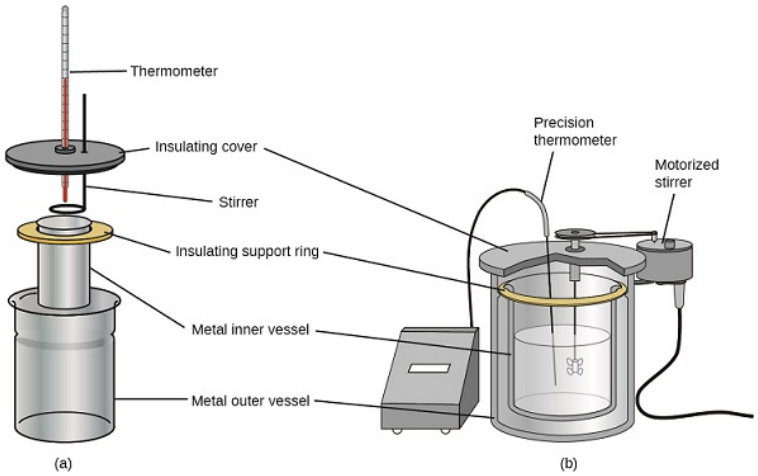


Figure **4.1.2.3**: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before we practice calorimetry problems involving chemical reactions, consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure **4.1.2.4**). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0$$

This relationship is sometimes rearranged to more explicitly show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

The magnitude of the heat (change) is the same for both substances, and the negative sign merely shows that $q_{\text{substance}}$ M and $q_{\text{substance}}$ W are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance}}$ M is a negative value and $q_{\text{substance}}$ W is positive, since heat is transferred from M to W.

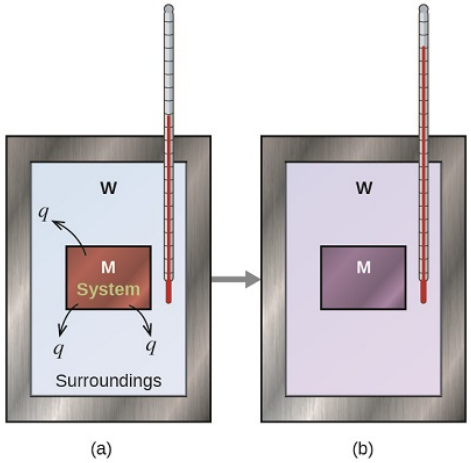


Figure **4.1.2.4**: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 4.1.2.1: Heat Transfer between Substances at Different Temperatures

A hot 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water is measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = − heat taken in by water, or:

$$q_{\text{rebar}} + q_{\text{water}} = 0$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} + (c \times m \times \Delta T)_{\text{water}} = 0$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) + c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) = 0$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g °C})(360\text{g})(42.7°\text{C} - T_{\text{i,rebar}}) + (4.184\ \text{J/g °C})(425\ \text{g})(42.7°\text{C} - 24.0°\text{C}) = 0$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g °C})(425\ \text{g})(42.7°\text{C} - 24.0°\text{C})}{(0.449\ \text{J/g °C})(360\ \text{g})} + 42.7°\text{C}$$

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 4.1.2.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

Exercise 4.1.2.1B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.7 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example 4.1.2.2: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal will be absorbed by the water, or:

$$q_{\text{metal}} + q_{\text{water}} = 0$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) + c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) = 0$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{metal})(59.7\ g)(28.5°C - 100.0°C) + (4.18\ J/g\ °C)(60.0\ g)(28.5°C - 22.0°C) = 0$$

Solving this:

$$c_{metal} = \frac{-(4.184\ J/g\ °C)(60.0\ g)(6.5°C)}{(59.7\ g)(-71.5°C)} = 0.38\ J/g\ °C$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 4.1.2.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$c_{metal} = 0.13\ J/g\ °C$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in an aqueous chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), $q_{reaction}$, plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero:

$$q_{reaction} + q_{solution} = 0 \qquad (4.1.2.1)$$

The amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution. This concept lies at the heart of all calorimetry problems and calculations.

Example 4.1.2.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(aq) and 50.0 mL of 1.00 M NaOH(aq), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{reaction} + q_{solution} = 0$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{solution} = (c \times m \times \Delta T)_{solution}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{solution} = (4.184\ J/g\ °C)(1.0 \times 10^2\ g)(28.9°C - 22.0°C) = 2.89 \times 10^3\ J$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{reaction} = -q_{solution} = -2.89 \times 10^3\ J$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

Exercise 4.1.2.3

When 100 mL of 0.200 M NaCl(aq) and 100 mL of 0.200 M $AgNO_3$(aq), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer

$1.34 \times 10^3\ J$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 4.1.2.5). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\mathbf{NaC_2H_3O_2}(aq) \longrightarrow \mathbf{NaC_2H_3O_2}(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.



Figure 4.1.2.5: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$\mathbf{2\,Fe}(s) + \frac{3}{2}\mathbf{O_2}(g) \longrightarrow \mathbf{Fe_2O_3}(s). \qquad (4.1.2.2)$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Example 4.1.2.4: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack” (Figure 4.1.2.5). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.



Figure **4.1.2.5**: An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{rxn} + q_{soln} = 0$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{rxn} &= -q_{soln} = -(c \times m \times \Delta T)_{soln} \\ &= -[(4.184\,J/g\,°C) \times (53.2\,g) \times (20.3°C - 24.9°C)] \\ &= -[(4.184\,J/g\,°C) \times (53.2\,g) \times (-4.6°C)] \\ &+ 1.0 \times 10^3\,J = +1.0\,kJ \end{aligned}$$

The positive sign for q indicates that the dissolution is an endothermic process.

Exercise 4.1.2.4

When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

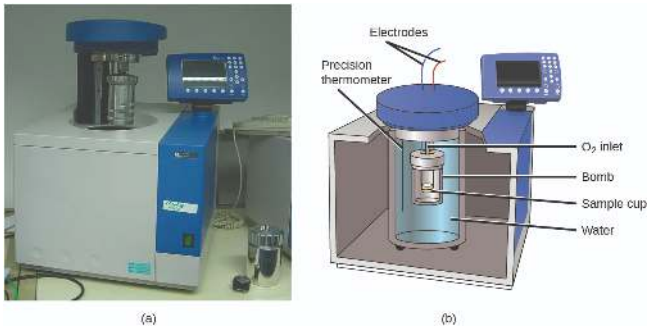
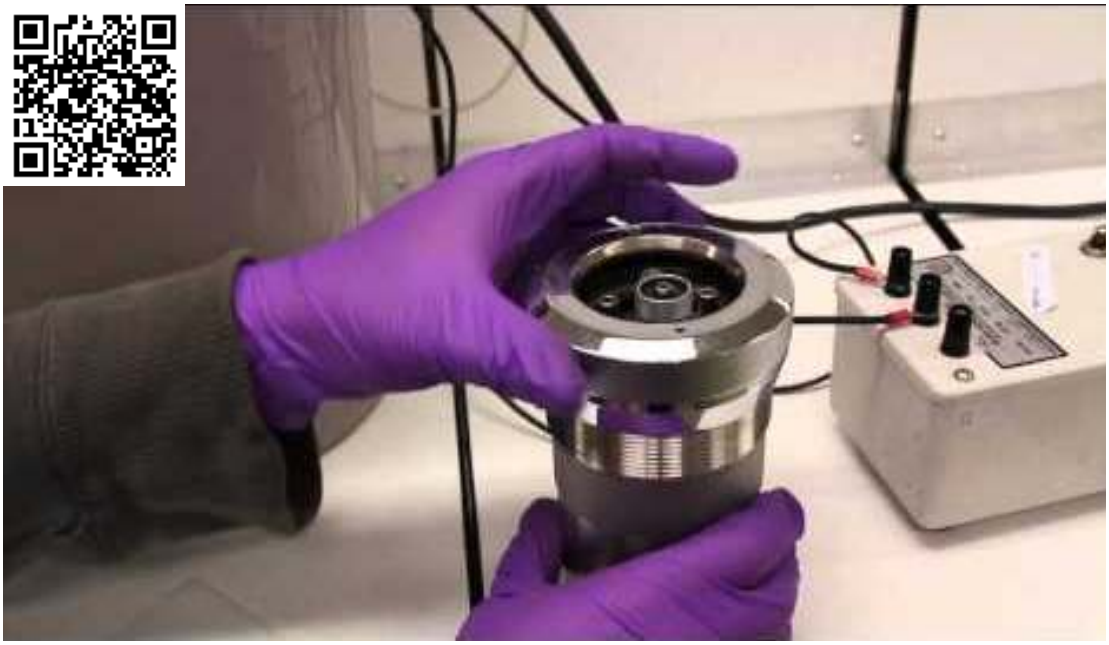


Figure **4.1.2.6**: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is

used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure **4.1.2.6**). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.



Video* 4.1.2.1*: *Video of view how a bomb calorimeter is prepared for action.*

Example 4.1.2.5: Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{rxn} &= -(q_{water} + q_{bomb}) \\ &= -[(4.184\ J/g\ °C) \times (775\ g) \times (35.6°C - 23.8°C) + 893\ J/°C \times (35.6°C - 23.8°C)] \\ &= -(38,300\ J + 10,500\ J) \\ &= -48,800\ J = -48.8\ kJ \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

Exercise 4.1.2.5

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Answer

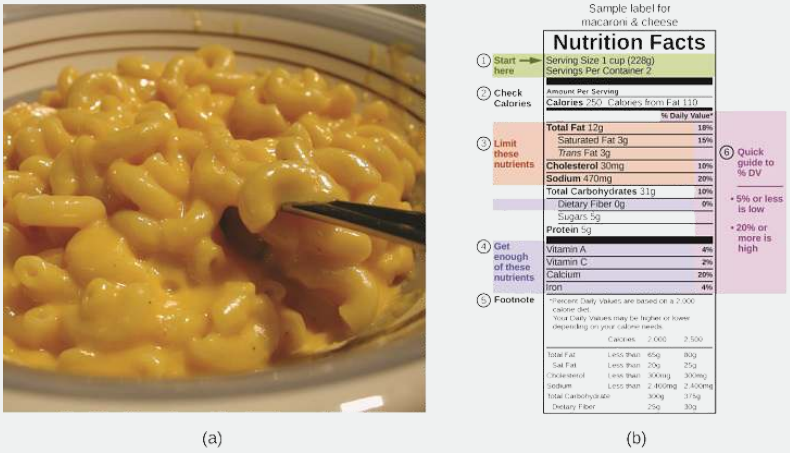
39.0 kJ

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[1] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure **4.1.2.7**).



(a) (b)

Figure **4.1.2.7**: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5\text{ g protein} \times 4\text{ Calories/g}) + (31\text{ g carb} \times 4\text{ Calories/g}) + (12\text{ g fat} \times 9\text{ Calories/g}) = 252\text{ Calories} \quad (4.1.2.3)$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations. Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Footnotes

1. 1 Francis D. Reardon et al. “The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics.” *Medical and Biological Engineering and Computing* 8 (2006)721–28, http://link.springer.com/article/10....517-006-0086-5.

Glossary

bomb calorimeter

device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter

device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry

process of measuring the amount of heat involved in a chemical or physical process

nutritional calorie (Calorie)

unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings

all matter other than the system being studied

system

portion of matter undergoing a chemical or physical change being studied

Contributors and Attributions

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4.1.3: The First Law of Thermodynamics

The First Law of Thermodynamics

One of the great achievements of the 19th century was the recognition that heat and work are two forms of the same thing (energy), and heat and work are the only ways in which we can transfer energy from one object to another. We can summarize these statements as follows:

> In any process, energy can never be created or destroyed; it can only be transferred from one object to another in the form of heat and/or work.

This statement is called the **First Law of Thermodynamics**, and it can also be written as a mathematical equation:

$$\Delta E = q + w \tag{4.1.3.1}$$

Where

ΔE is the change in the internal energy of a system (a collection of matter)

q is the amount of heat transferred into or out of the system

w is the amount of work that is done on or by the system

First Law of Thermodynamics and the Law of Conservation of Energy

The first law of thermodynamics is actually the law of conservation of energy stated in a form most useful in thermodynamics. The first law gives the relationship between heat transfer, work done, and the change in internal energy of a system.

Here are three examples. Note that in each case, we must be careful to specify our system before we assign signs to q and w.

- *You heat a beaker of water:* If we choose the water to be our system, q is a positive number, because the heat is moving into the water. The energy of the water increases when we heat it, so ΔE is positive, and q must agree with this.
- *You lift a suitcase:* If we consider you to be the system, w is a negative number, because you are doing the work. Your body's energy decreases as you lift the suitcase, so ΔE is negative, and w must agree with this. On the other hand, if we consider the suitcase to be the system, w is a positive number, because the surroundings are doing the work on the suitcase. (If you aren't the system, you are part of the surroundings.)
- *You drop an ice cube into a beaker of hot water:* If we consider the ice cube to be the system, q is a positive number, because the ice cube absorbs heat (and gains energy). If we consider the hot water to be the system. q is a negative number, because the water loses heat (and loses energy).

Heat and Work in the First Law

Heat q and **work** w are the two everyday means of bringing energy into or taking energy out of a system. The processes are quite different. Heat transfer, a disorganized process, is driven by temperature differences. Work, a quite organized process, involves a macroscopic force exerted through a distance. Nevertheless, heat and work can produce identical results. For example, both can cause a temperature increase. Heat transfer into a system, such as when the Sun warms the air in a bicycle tire, can increase its temperature, and so can work done on the system, as when the bicyclist pumps air into the tire. Once the temperature increase has occurred, it is impossible to tell whether it was caused by heat transfer or by doing work. This uncertainty is an important point. Heat and work are both energy in transit—neither is stored as such in a system. However, both can change the internal energy E of a system.

Internal Energy in the First Law

The **internal energy** E of a system is the sum of the kinetic and potential energies of its atoms and molecules. Because it is impossible to keep track of all individual atoms and molecules, we must deal with averages and distributions.

The internal energy E of a system depends only on the state of the system and *not how it reached that state*. More specifically, E is found to be a function of a few macroscopic quantities (pressure, volume, and temperature, for example), independent of past history such as whether there has been heat transfer or work done. This independence means that if we know the state of a system, we can calculate changes in its internal energy U from a few macroscopic variables.

To get a better idea of how to think about the internal energy of a system, let us examine a system going from State 1 to State 2. The system has internal energy E_1 in State 1, and it has internal energy E_2 in State 2, no matter how it got to either state. So the change in internal energy

$$\Delta E = E_2 - E_1 \tag{4.1.3.2}$$

is independent of what caused the change. In other words, δE *is independent of path*. By path, we mean the method of getting from the starting point to the ending point. Why is this independence important? Both q and w *depend on path*, but ΔE does not (Equation 6.3.1). This path independence means that internal energy E is easier to consider than either heat transfer or work done.

Example 4.1.3.1: Calculating Change in Internal Energy - The Same Change in E is Produced by Two Different Processes

Question:

a. Suppose there is heat transfer of 40.00 J to a system, while the system does 10.00 J of work. Later, there is heat transfer of 25.00 J out of the system while 4.00 J of work is done on the system. What is the net change in internal energy of the system?

b. What is the change in internal energy of a system when a total of 150.00 J of heat transfer occurs out of (from) the system and 159.00 J of work is done on the system

Strategy:

In part (a), we must first find the net heat transfer and net work done from the given information. Then the first law of thermodynamics (Equation 6.3.1).

can be used to find the change in internal energy. In part (b), the net heat transfer and work done are given, so the equation can be used directly.

Solution for (a)

The net heat transfer is the heat transfer into the system minus the heat transfer out of the system, or

$$q = q_{in} + q_{out} = 40.00J + (-25.00J) = 15.00J$$

Similarly, the total work is the work done by the system minus the work done on the system, or

$$w = w_{in} + q_{out} = 4.00J + (-10.00J) = -6.00J$$

Adding the net heat transfer and total work gives

$$\Delta E = q + w = 15J + (-6.00J) = 9.00J.$$

Solution for (b)

Here the net heat transfer and total work are given directly to be $q = -150.00J$ and $w = +159.00J$, so that

$$\Delta E = q + w = -150.00 + 159.00 = 9.00J$$

Discussion

A very different process in part (b) produces the same 9.00-J change in internal energy as in part (a). Note that the change in the system in both parts is related to ΔE and not to the individual qs or ws involved. The system ends up in the *same* state in both (a) and (b). Parts (a) and (b) present two different paths for the system to follow between the same starting and ending points, and the change in internal energy for each is the same—it is independent of path.

Summary

The table presents a summary of terms relevant to the first law of thermodynamics.

Term	Definition
E	Internal energy—the sum of the kinetic and potential energies of a system's atoms and molecules. Can be divided into many subcategories, such as thermal and chemical energy. Depends only on the state of a system (such as its P, V and T, not on how the energy entered the system. Change in internal energy is path independent.
q	Heat—energy transferred because of a temperature difference. Characterized by random molecular motion. Highly dependent on path. q entering a system is positive.
w	Work—energy transferred by a force moving through a distance. An organized, orderly process. Path dependent. w done by a system (either against an external force or to increase the volume of the system) is positive.

- The first law of thermodynamics is given as $\Delta E = q + w$, where ΔE is the change in internal energy of a system, q is the net heat transfer (the sum of all heat transfer into and out of the system), and w is the net work done (the sum of all work done on or by the system).
- Both q and w are energy in transit; only ΔE represents an independent quantity capable of being stored.
- The internal energy E of a system depends only on the state of the system and not how it reached that state.

Glossary

first law of thermodynamics

states that the change in internal energy of a system equals the net heat transfer *into* the system minus the net work done *by* the system

internal energy

the sum of the kinetic and potential energies of a system's atoms and molecules

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4.1.4: Energy and Chemical Change

Potential Energy and Kinetic Energy for a Chemical System

Any collection of matter has two types of energy, **kinetic energy** and **potential energy**. These types of energy are defined as follows:

- *Kinetic energy is the energy an object has because it is moving.*
- *Potential energy is the energy an object has because of its position.*

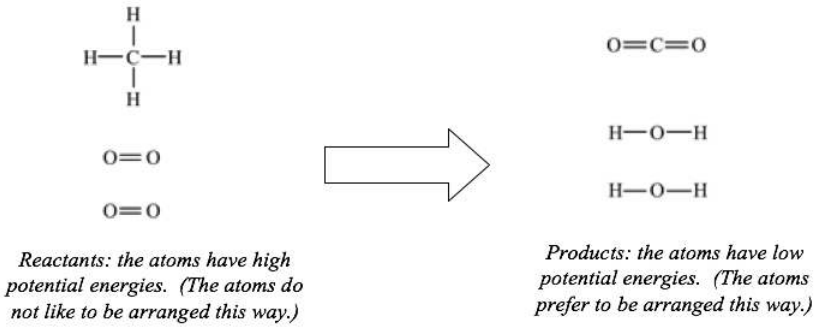
For example, a rolling ball has energy because it is moving; it can do work if it hits something. A stationary ball that is high in the air also has energy, it can do work if it is allowed to fall.

In chemistry, we are primarily concerned with **thermal energy** and **chemical energy**. Thermal energy is the energy in a hot object; a hot piece of metal has more energy than a cold piece of metal. Thermal energy is due to the motion of the atoms in the object; in a hot object, the atoms are moving rapidly, whereas in a cold object they are moving more slowly. Since this energy is due to motion, *thermal energy is a type of kinetic energy*.

Chemical energy is the energy that will be released or absorbed when chemicals react with one another. For example, Bunsen burners (and gas applicances) use the reaction between CH_4 (methane, the primary constituent of natural gas) and O_2 to produce heat:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$$

If you mix some CH_4 and some oxygen at room temperature, the mixture will remain unchanged indefinitely. However, if you strike a spark, the two gases react violently, producing a great deal of thermal energy. This thermal energy does not "come from nowhere"; it was originally stored in the CH_4 and O_2 molecules. This stored energy is undetectable to us until the reaction occurs; a mixture of CH_4 and O_2 looks just like a mixture of He and Ne (which cannot react with one another and have no stored energy). The energy that is stored in a mixture of CH_4 and O_2 is chemical energy, and it is due to the positions of the atoms. In this reaction, the atoms have lower potential energies when the oxygen atoms are bonded to carbon and hydrogen, rather than to each other, as shown below.



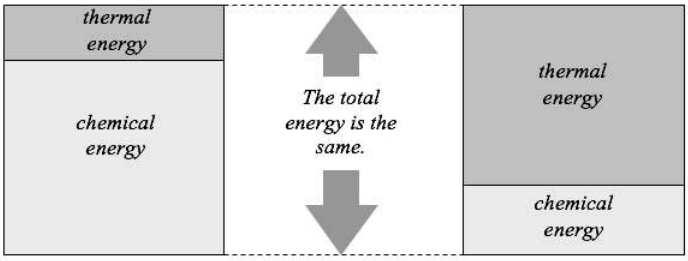
Reactants: the atoms have high potential energies. (The atoms do not like to be arranged this way.)

Products: the atoms have low potential energies. (The atoms prefer to be arranged this way.)

Since chemical energy depends on positions of atoms, *chemical energy is a type of potential energy*. Chemical energy does not depend on temperature.

Energy transfers and and chemical reactions

Most reactions that we encounter produce thermal energy; the reacting chemicals, and everything around them, become hot. Any reaction that produces thermal energy is called **exothermic**. In an exothermic reaction, heat seems to come from nowhere. However, no process can simply create energy, because doing so would violate the principle of conservation of energy. Instead, *exothermic reactions convert chemical energy into thermal energy.* This thermal energy is then transferred from the reaction products to the surroundings. We can illustrate this conversion graphically as shown below.



*The **reactants** don't have much thermal energy (they are cool), but they have a lot of chemical energy.*

*The **products** don't have much chemical energy, but they have a lot of thermal energy (they are hot).*

As you can see from the figure, the overall energy change in any reaction is zero; energy is neither created nor destroyed. However, the amount of chemical energy changes in any reaction; the products never contain the same amount of chemical energy as the reactants do. *When chemists talk about the "energy of a reaction," they always mean the change in the chemical energy.*

Here is a simple example of how we might measure the energy of a reaction. Suppose that we carry out the reaction in a container that is surrounded by water. After the reaction, we find that the water is hotter; and by measuring the temperature change and the mass, we find that the water has absorbed 50 kJ of heat. From the standpoint of the water, the heat is a positive number, since the water gained energy. We can write

q_{water} = + 50 kJ

where the subscript "water" means that the water is our system (for the moment).

Now, our real interest is in the chemical reaction. Recall the the First Law of Thermodynamics: *In any process, energy can never be created or destroyed; it can only be transferred from one object to another in the form of heat and/or work.* Or, stated as a mathematical equation: $\Delta E = q + w$. The First Law tells us that the heat that went into the water must have come out of the reacting chemicals, so the reacting chemicals must have lost 50 kJ of heat. From the standpoint of the chemicals, the heat is a negative number. We can write:

$q_{chemicals}$ = -50 kJ

We did not allow any work to be done, so $w_{chemicals} = 0$. Now we can use the First Law of Thermodynamics to calculate the energy change that occurred in the chemicals.

$$\Delta E_{chemicals} = q_{chemicals} + w_{chemicals}$$

$$= (-50 \text{ kJ}) + 0 \text{ kJ}$$

$$= -50 \text{ kJ}$$

The energy of the chemicals decreased by 50 kJ during the reaction. This ΔE is the change in the chemical energy; the reactants had 50 kJ more potential energy than the products did. Note that the value of ΔE is negative; ΔE *is negative for an exothermic reaction.*

Some reactions consume thermal energy. In this type of reaction, called an **endothermic** reaction, the chemicals and their surroundings become colder. *Endothermic reactions convert thermal energy into chemical energy*. Since the chemical energy cannot be felt or detected, these reactions seem to make energy disappear. For an endothermic reaction, all of the signs we saw above are reversed. For instance, suppose that we carry out a reaction in a container that is surrounded by water, and after the reaction we find that the water has become colder. By measuring the temperature change and the mass, we find that the water has lost 30 kJ of heat. From the standpoint of the water, then, q = -30 kJ. This heat was absorbed by the reacting chemicals, so from the standpoint of the chemicals, q = +30 kJ. By the First Law of Thermodynamics, ΔE = +30 kJ for this reaction. The products have 30 kJ more chemical energy than the reactants had. ΔE *is positive for an endothermic reaction.*

Here is a summary of the differences between exothermic and endothermic reactions:

In an exothermic reaction:

- Everything gets warmer.
- The reaction changes chemical energy into thermal energy.
- q is positive for the surroundings.
- q is negative for the chemicals.
- ΔE is negative.

In an endothermic reaction:

- Everything gets colder.
- The reaction changes thermal energy into chemical energy.
- q is negative for the surroundings.
- q is positive for the chemicals.
- ΔE is positive.

Energy and Reaction Stoichiometry

The amount of energy that a reaction produces or absorbs depends on the amounts of chemicals that react. This should seem obvious; for instance, two gallons of gasoline produce twice as much heat as one gallon of gasoline. When chemists report ΔE values for a reaction, they must therefore specify the amounts of chemicals that were used. There are two ways that chemists do this.

Option 1: Give the energy on a per mole (or per gram) basis, based on the most important chemical.

This option is used for physical processes that involve one chemical (such as evaporation or dissolving), and it is also commonly used for combustion reactions. For example, a chemist might say that ΔE = -884.7 kJ/mol for the combustion of CH_4(g). This statement tells us that if we allow one mole of CH_4 to react with excess oxygen, we will get 884.7 kJ of energy. The negative sign of DE tells us that the chemical energy decreases by 884.7 kJ. This chemical energy is changed into thermal energy, so the chemicals create 884.7 kJ of thermal energy.

Option 2: Give a balanced chemical equation, and give the energy that is produced by the numbers of moles in the chemical equation.

This is the most common option. For instance, we might see the following statement:

$$2\,Ag^+(aq) + S^{2-}(aq) \longrightarrow Ag_2S(s) \qquad \Delta E = -277kJ$$

This statement tells us that when 2 moles of Ag^+(aq) reacts with 1 mole of S^{2-}(aq), we get 277 kJ of energy. We would not write "ΔE = -277 kJ/mol for the reaction of Ag^+ and S^{2-}", because the unit "kJ/mol" implies "kilojoules per one mole", but we must use two moles of Ag^+ to get our 277 kJ of energy.*

The ratio of energy to moles is a constant for any reaction. This fact allows us to calculate the energy change (and therefore the heat) when any amount of a chemical reacts. For instance, suppose that we react 0.25 mol of $AgNO_3$(aq) with excess Na_2S. We can set up the following proportionality:

$$\frac{-277\text{ kJ}}{2\text{ mol AgNO}_3} = \frac{\Delta E}{0.25\text{ mol AgNO}_3}$$

The values in the left-hand fraction come from the balanced equation above: we get 277 kJ of energy when we use 2 moles of $AgNO_3$. The ΔE in the right-hand fraction represents the energy we get when we use 0.25 moles of $AgNO_3$. Solving this equation gives us ΔE = -34.6 kJ, so we get 34.6 kJ of energy when 0.25 mol of $AgNO_3$(aq) reacts with excess Na_2S(aq).

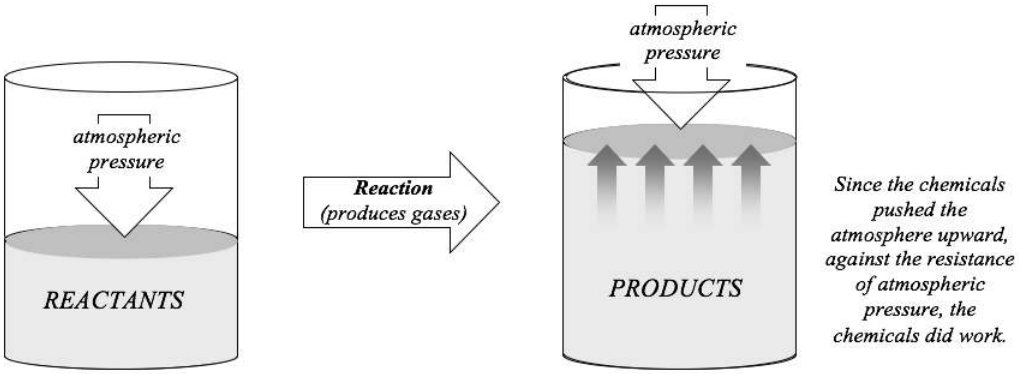
PV work

The most practical way to measure ΔE for a reaction is to carry out the reaction under conditions in which all of the energy is produced in the form of heat, because heat is much easier to measure than work. For most reactions, this is simple enough; most

reactions will not do work unless the energy of the reaction is harnessed by some sort of machine. However, reactions that produce or consume gases are an exception. If the reaction produces a gas, the gas must push the atmosphere out of the way to make room for itself. This "pushing the atmosphere out of the way" involves motion (the reaction mixture expands) against a resistance (the atmospheric pressure), so it is work. The work that is done is given by the expression:

$w = -P_{external} \times \Delta V$

where $P_{external}$ is the pressure exerted by the surrounding atmosphere, and ΔV is the change in the volume of the reaction mixture as it produces the gas. The negative sign is needed because the reaction mixture is doing the work; remember that when a system does work, its energy decreases. The figure below illustrates this type of work.



If a reaction consumes a gas, the reaction mixture becomes smaller as the gas is consumed, and the surrounding atmosphere must push inward to fill the empty space. In this case, the atmosphere does the work, but the equation

$w = -P_{external} \times \Delta V$

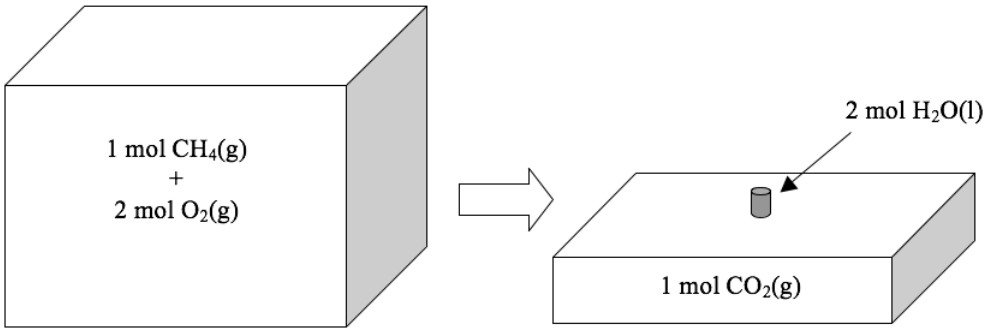
still applies. In this case, ΔV is a negative number when the reaction mixture contracts, while w is positive, reflecting the fact that the surroundings are doing the work.

These types of work are called **PV work**, and they occur whenever we carry out a reaction that involves gas production or consumption in an open container. Therefore, if we want to ensure that no work is done during a reaction, *we must carry out the reaction in a sealed container that cannot expand or contract.* As long as the volume of the reaction mixture is constant, no PV work can be done. If the reaction produces a gas, the gas must squeeze itself into the existing space, but it cannot do work, because it cannot move the walls of the container. (Remember that work requires motion: if nothing moves, there is no work.) If the reaction consumes a gas, it will decrease the pressure in the container, but the surrounding atmosphere cannot collapse the walls of the container to equalize the pressures, so again, there is no work.

Whenever a reaction does PV work, the amount of heat that it produces or absorbs will be different from ΔE, because ΔE equals the heat only when w = 0. For example, if we burn one mole of CH_4 in an open container, the reaction produces 884.7 kJ of energy (as we saw above), but we get 889.7 kJ of heat from the reaction. At first glance, this seems impossible; how can the heat be larger than the overall energy? However, if we go back and look at the balanced equation…

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

…we see that this reaction converts three moles of gases (one mole of CH_4 plus two moles of O_2) into one mole of a gas (CO_2) plus two moles of a liquid (H_2O). Liquids have vastly smaller volumes than gases; at 25ºC and 1 atm, a mole of any gas occupies about 24.5 L under these conditions, whereas a mole of liquid water occupies just 0.018 L. Therefore, the total volume of the reaction mixture decreases, as shown below.



Note that the reaction mixture will not shrink on its own; the atmosphere must push inward and force the reaction mixture to become smaller. As the atmosphere compresses the reaction mixture, it does work. If the reaction occurred in a flexible container, we could see this work being done; for example, if the reaction took place in a balloon, the balloon would shrink dramatically. However, this work occurs whenever the external pressure is constant, regardless of whether we can see it.

In our example here, the atmosphere does 5.0 kJ of work. (You'll see how to calculate this in a moment.) Since the surroundings are doing the work, w is a positive value from the standpoint of the reaction mixture; $w_{reaction}$ = +5.0 kJ. The First Law then governs the amount of heat we obtain:

$\Delta E_{reaction} = q_{reaction} + w_{reaction}$

-884.7 kJ = $q_{reaction}$ + 5.0 kJ

$q_{reaction}$ = -889.7 kJ

The physical meaning of these numbers is that the reaction converts 884.7 kJ of chemical energy into thermal energy, which comes out in the form of heat. The surrounding atmosphere contributes an additional 5.0 kJ as it compresses the reaction mixture. The reaction mixture converts this work into additional heat, so we get a total of 889.7 kJ of heat.

We can calculate the PV work using the equation $w_{PV} = -P_{external} \times \Delta V$. However, a much more convenient expression can be derived using the ideal gas law. To do so, we make a few assumptions:

- The internal pressure is essentially equal to the external pressure at all times, and the internal pressure is due entirely to the gases in the reaction mixture.
- The final temperature equals the initial temperature (which is reasonable if we want to extract all of the heat from a reaction).
- The volumes of any solids and liquids are so much smaller than the volumes of the gases that we can ignore them. We also make the substitution $\Delta V = V_{final} - V_{initial}$.

Using these assumptions, we get:

$$w_{PV} = -P\Delta V$$

$$= -(PV_{final} - PV_{initial})$$

$$= -(RTn_{final} - RTn_{initial})$$

$$= -RT(n_{final} - n_{initial})$$

$$= -RTDn_{gases}$$

$$\boldsymbol{w_{PV} = -RT\Delta n_{gases}}$$

By this derivation, we see that when the pressure remains constant, the PV work depends only on the temperature and the change in the number of moles of gases during the reaction. To get our value of w_{PV} in joules, we must use R = 8.314 J/mol·K.

For example, here is how we would calculate the PV work for the combustion of one mole of CH_4 at constant pressure. The balanced equation is:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$

The reaction converts 3 moles of gaseous reactants into 1 mole of gaseous product (plus some liquid water, which we ignore). Therefore, Δn_{gases} = 1 mol – 3 mol = -2 mol. Using T = 298 K (25ºC), we get:

w_{PV} = -(8.314 J/mol·K)(298 K)(-2 mol) = 4955 J = 4.955 kJ ≈ 5.0 kJ*

It is worth noting that *PV work can only occur if a reaction produces more or fewer moles of gas than it consumes*.** Many reactions do not involve gases at all, including precipitation reactions and acid-base reactions. A few reactions produce the same number of moles of gases that they consume, so the volume does not change. Here is an example:

$C(s) + O_2(g) \rightarrow CO_2(g)$

**If we know the values of P and V, we can also calculate the PV work by multiplying P x ΔV, then using the conversion 1 L·atm = 101.325 J.*

***Strictly, a tiny amount of PV work occurs even when a reaction involves only solids and liquids, but this PV work is so small that it does not produce a detectable change in the heat.*

This reaction consumes a mole of gas (the O_2) and produces a mole of gas (the CO_2), so there is no change in the total number of moles of gases (Δn_{gases} = 0) and therefore no PV work. This situation is uncommon, though; for most reactions that involve gases, the number of moles of gases changes during the reaction, so PV work can occur.

The amount of PV work that will occur during a reaction is typically much smaller than ΔE for the reaction, so ignoring it doesn't usually introduce a very large error. Here are a few examples of reactions involving gases, with their ΔE and w_{PV} values (calculated at room temperature, 298 K). Only for the last reaction is w_{PV} a significant fraction of the overall energy change.

$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$	ΔE = -563.5 kJ	w_{PV} = +2.5 kJ (0.4% of ΔE)
$2\ Al(s) + 6\ HCl(aq) \rightarrow 2\ AlCl_3(aq) + 3\ H_2(g)$	ΔE = -1063 kJ	w_{PV} = -7.5 kJ (0.7% of ΔE)
$P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$	ΔE = -2984 kJ	w_{PV} = +12.5 kJ (0.4% of ΔE)
$CO_2(g) + NaOH(aq) \rightarrow NaHCO_3(aq)$	ΔE = -66.0 kJ	w_{PV} = +2.5 kJ (4% of ΔE)

For most of these reactions, ignoring the PV work and assuming that all of the energy is transferred in the form of heat would not produce a significant error. However, chemists do not like to introduce errors into their work if they can avoid it. As we saw earlier, we can eliminate PV work by using a sealed, rigid container to carry out reactions that involve gases. Unfortunately, while carrying out reactions in sealed, rigid containers is feasible, it is not particularly practical for most applications. If we want to use a chemical reaction to heat our homes, or to power an engine, or to make a useful product, we need to expose the reaction mixture to the surroundings, and doing so allows PV work to occur. As a result, PV work presents an annoying complication whenever we want to calculate the heat that a reaction will give off or absorb.

Next, we will look at how chemists get around this problem…

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4.1.5: Enthalpy – A Modified Energy of Reaction

Enthalpy

To avoid having to constantly calculate and compensate for PV work when they are carrying out reactions involving gases, chemists created a modified measure of the energy produced or consumed in a reaction. This measure is called **enthalpy** and given the symbol H. Enthalpy is defined as follows:

$H = E + PV$

Here, E is the chemical energy of a substance, and P and V are the pressure and volume of the substance. To calculate a value of H for a substance, we would need to know the value of E. Since it isn't possible to measure internal energy, we can never calculate or measure the enthalpy of a substance. However, we can measure the change in the internal energy of a substance, so we can also measure changes in enthalpy.

For instance, suppose we wanted to know the change in enthalpy (ΔH) when we convert two moles of NO_2 into one mole of N_2O_4. The chemical equation is:

$2\ NO_2(g) \text{ --> } N_2O_4(g)$

For this reaction, E is -54.72 kJ. What is (ΔH)? To find a way to calculate DH, let us start with some algebra, remembering that H = E + PV and (ΔH) = $H_{final} - H_{initial}$…

$\Delta H = H_{final} - H_{initial}$

$\Delta H = (E + PV)_{final} - (E + PV)_{initial}$

$\Delta H = (E_{final} + P_{final}V_{final}) - (E_{initial} + P_{initial}V_{initial})$

$\Delta H = (E_{final} - E_{initial}) + (P_{final}V_{final} - P_{initial}V_{initial})$

$\Delta H = \Delta E + (P_{final}V_{final} - P_{initial}V_{initial})$

The last equation tells us that we can calculate ΔH if we can calculate the product P x V before and after the reaction. Since all of the chemicals are gases, we can use PV = nRT, but we still need to know the temperature. ΔE is normally measured at 25ºC (298 K), so let's calculate ΔH at 298 K. Making the substitution PV = nRT gives us…

$\Delta H = \Delta E + (n_{final}RT - n_{initial}RT)$

$\Delta H = \Delta E + RT(n_{final} - n_{initial})$

According to the balanced equation, the reaction converts two moles of gaseous NO_2 into one mole of gaseous N_2O_4, so we can now calculate (ΔH):

ΔH = -54.72 kJ + (8.314 J/mol·K)(298 K)(1 mol – 2 mol)

ΔH = -54.72 kJ + (-2478 J)

ΔH = -54.72 kJ + (-2.478 kJ)

ΔH = -57.20 kJ

This value of ΔH is a combination of two physical effects. First, the internal energy of the chemicals decreases by 54.72 kJ when two moles of NO_2 combine to form one mole of N_2O_4. Second, the value of PV decreases by 2.478 kJ when two moles of NO_2 combine to form one mole of N_2O_4. This makes sense; when the number of moles of gas decreases, the volume or the pressure (or both) must drop.

Why do chemists use change in enthalpy (ΔH) more often than (ΔE)?

What is the utility of combining internal energy and PV? The answer is that when the pressure is constant, the expression ($P_{final}V_{final} - P_{initial}V_{initial}$) equals the PV work, but with the opposite sign. Here's how we can prove it:

If the pressure is constant, $P_{initial} = P_{final}$

So we can just write "P" in place of both $P_{initial}$ and P_{final}

Then ($P_{final}V_{final} - P_{initial}V_{initial}$) becomes ($PV_{final} - PV_{initial}$)

Factoring out P gives us $P(V_{final} - V_{initial})$

But $V_{final} - V_{initial}$ is an expanded way to write (ΔV)

So ($P_{final}V_{final} - P_{initial}V_{initial}$) = $P(\Delta V)$

The PV work is given by the expression $w_{PV} = -P(\Delta V)$

So $\mathbf{(P_{final}V_{final} - P_{initial}V_{initial}) = -w_{PV}}$

Earlier, we saw that

$\Delta H = \Delta E + (P_{final}V_{final} - P_{initial}V_{initial})$

So, after all of this algebra, we reach the following statement

If the pressure is constant, $\Delta H = \Delta E + (-w_{PV})$

Now, let's bring back the First Law of Thermodynamics, which tells us that (ΔE) = q + w. Substituting this expression for ΔE gives us:

If the pressure is constant, $\Delta H = (q + w) + (-w_{PV})$

Simplifying this equation, $\Delta H = q + (w - w_{PV})$ where *w* is all types of work and w_{PV} is specifically PV work, meaning that the difference ($w - w_{PV}$) is really just any work that is done *other than* PV work. Substituting (w_{other}) into the equation, we arrive at the following statement:

***If the pressure is constant,* $\Delta H = q + w_{other}$**

And, as long as we don't run our reaction in some sort of machine or battery, etc., *then no other work will be done* ($w_{other} = 0$) and the above equation reduced to:

> ***If the pressure is constant, and no work other than PV work is done,***
>
> $\Delta H = q$

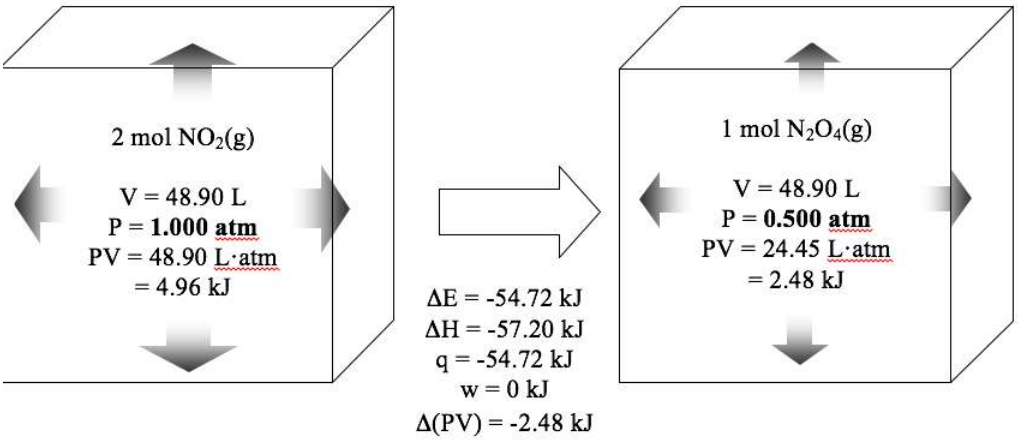
This is why chemists "invented" enthalpy. *When the pressure is constant, the* ΔH *for a reaction tells us the amount of heat the reaction will produce or absorb.* We no longer have to calculate PV work. Remember that "constant pressure" simply means that the reaction occurs in an open container, so the chemical mixture is free to expand or contract. Since we carry out most reactions under these conditions, chemists normally use ΔH instead of ΔE to describe the energy given off or absorbed by a reaction.

Let's put this idea into practice. A while ago, we looked at the reaction 2 $NO_2(g)$ --> $N_2O_4(g)$, and we found that for this reaction, ΔE = -54.72 kJ and ΔH = -57.20 kJ. What do these numbers tell us?

- If we carry out the reaction in a sealed, rigid container, the amount of heat we get will equal ΔE: we will get 54.72 kJ of heat.
- If we carry out the reaction in an open container, the amount of heat we get will equal ΔH: we will get 57.20 kJ of heat.

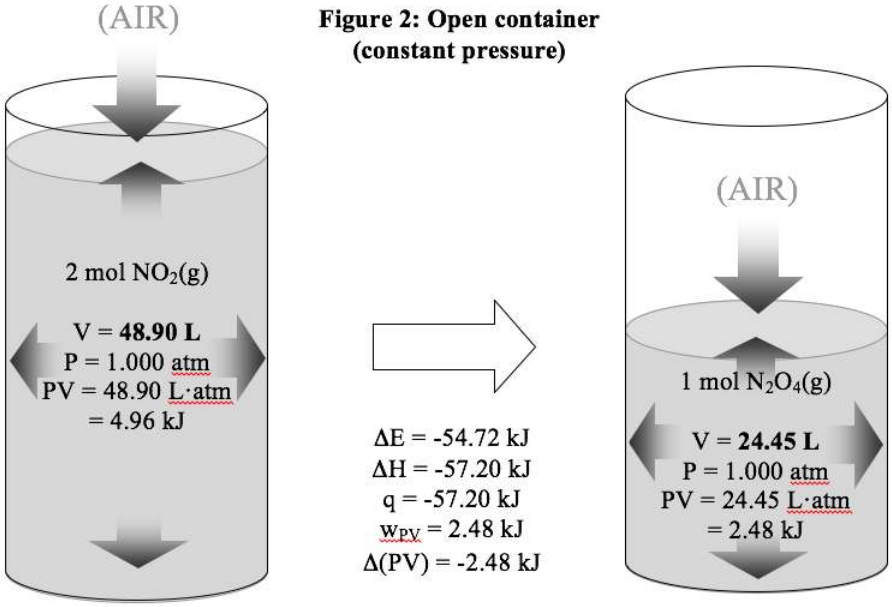
It is important to recognize that *the values of* ΔE *and* ΔH *do not depend on whether we carry out the reaction in an open or closed container.* For this reaction, ΔH is -57.20 kJ even if the reaction occurs in a sealed, rigid container. However, under these conditions, ΔH does not equal the heat. In fact, ΔH doesn't really mean anything very useful when we are in a sealed, rigid container. All it tells us is that the quantity (E + PV) is decreasing by 57.20 kJ. Since E itself decreases by 54.72 kJ, the product P·V decreases by 2.48 kJ (we can write this as $\Delta(PV) = -2.48$ kJ). In a sealed, rigid container, P·V changes because P changes while V stays constant; since V is constant, there is no PV work. In an open container, P·V changes because V changes while P stays constant; in this case, there is PV work. The following two figures compare the two ways of running the reaction.

Figure 1: Sealed, rigid container (constant volume)



When the volume is constant: P·V changes, but V does not change, so no PV work occurs.

Figure 2: Open container (constant pressure)



When the pressure is constant: V changes, so PV work occurs.
$\Delta(PV) = -w_{PV}$

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the

amount of heat associated with the reaction involving the number of moles of reactants and products as shown in the chemical equation. For example, consider this equation:

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)} \quad \Delta H = -286\ \mathrm{kJ} \tag{4.1.5.1}$$

This equation indicates that when 1 mole of hydrogen gas and 12 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property).

$$\begin{array}{l}\text{(two-fold increase in amounts)}\\ 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l) \quad \Delta H = 2 \times (-286\ \mathrm{kJ}) = -572\ \mathrm{kJ}\\ \text{(two-fold decrease in amounts)}\\ \frac{1}{2}\mathrm{H_2}(g) + \frac{1}{4}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{H_2O}(l) \quad \Delta H = \frac{1}{2} \times (-286\ \mathrm{kJ}) = -143\ \mathrm{kJ}\end{array}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 1/2 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} \quad \Delta H = -242\ k\,\mathrm{J} \tag{4.1.5.2}$$

3. A negative value of an enthalpy change, Δ*H*, indicates an exothermic reaction; a positive value of Δ*H* indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its Δ*H* is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Example 4.1.5.1: Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is ΔH, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described ?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1\ \cancel{\mathrm{mol\ HCl}} \times \frac{-2.9\ \mathrm{kJ}}{0.0500\ \cancel{\mathrm{mol\ HCl}}} = -58\ \mathrm{kJ}$$

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

\[\ce{HCl(aq)+NaOH(aq) \rightarrow NaCl(aq)+H2O(l) \;\;\; ΔH=\mathrm{−58\;kJ} \nonumber\]

Exercise 4.1.5.1

When 1.34 g Zn(s) reacts with 60.0 mL of 0.750 M HCl(aq), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \rightarrow ZnCl\,(aq) + H_2\,(g)}$$

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

Example 4.1.5.2: Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$\mathbf{C_{12}H_{22}O_{11}\,(aq) + 8\,KClO_3\,(aq) \rightarrow 12\,CO_2\,(g) + 11\,H_2O\,(l) + 8\,KCl\,(aq)}$$

Solution

We have $\mathbf{2.67\ \cancel{g} \times \frac{1\ mol}{342.3\ \cancel{g}} = 0.00780\ mol\ C_{12}H_{22}O_{11}}$ available, and

$\mathbf{7.19\ \cancel{g} \times \frac{1\ mol}{122.5\ \cancel{g}} = 0.0587\ mol\ KClO_3}$ available.

Since

$$\mathbf{0.0587\ mol\ KClO_3 \times \frac{1\ mol\ C_{12}H_{22}O_{11}}{8\ mol\ KClO_3} = 0.00734\ mol\ C_{12}H_{22}O_{11}}$$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\mathbf{\frac{-43.7\ kJ}{0.0587\ mol\ KClO_3}}$, so we have $\mathbf{\Delta H = 8\ mol \times \frac{-43.7\ kJ}{0.0587\ mol\ KClO_3} = -5960\ kJ}$. The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$\mathbf{C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\ kJ}$$

Exercise 4.1.5.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $\mathbf{FeCl_{2(s)}}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $\mathbf{FeCl_2\,(s)}$ is produced?

Answer

ΔH = −338 kJ

Relating ΔH to ΔE

The formal relationship between ΔH and ΔE is $\Delta H = \Delta E + \Delta(PV)$. However, we do not normally use this equation, because we do not specify the pressure and volume. As we did on page 11, we assume that any change in volume is due to a change in the number of moles of gases, so we make the substitution PV = nRT. We also assume constant temperature. This allows us to factor out R and T as shown below:

$\Delta H = \Delta E + \Delta(PV)$

$\Delta H = \Delta E + (P_{final}V_{final} - P_{initial}V_{initial})$

$\Delta H = \Delta E + (n_{final}RT - n_{initial}RT)$

$\Delta H = \Delta E + RT(n_{final} - n_{initial})$

$$\mathbf{\Delta H = \Delta E + RT\Delta n_{gases}}$$

We can use this equation to translate ΔH into ΔE (and vice versa), regardless of the actual pressure and volume. All we need to know is the temperature (which must be given to us) and the change in the number of moles of gases, which we can get using stoichiometry.

Example 4.1.5.3: Calculating ΔH given ΔE

For instance, suppose we know that ΔE = -918.2 kJ for the following reaction at 298 K:

$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(l)$

What is ΔH for this reaction at 298 K? We can use the relationship between ΔH and ΔE; all we need to do is determine the change in the number of moles of gases. This reaction converts 7 moles of gaseous reactants (4 moles of NH_3 and 3 moles of O_2) into 2 moles of gaseous products (the N_2), so \(\Delta n_{gases}\) = 2 mol – 7 mol = -5 mol.

ΔH = -918.2 kJ + (8.314 J/mol·K)(298 K)(-5 mol)

= -918.2 kJ + (-12388 J)

= -918.2 kJ + (-12.4 kJ)

= -930.6 kJ

Easy enough, eh? Just be sure that you pay attention to units; ΔH and ΔE are normally given in kJ, but the $RT\Delta n_{gases}$ term is in joules and must be converted to kJ.

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4.1.6: Putting it All Together

Relating Nonstandard Values of ΔH and ΔE

In many problems, you will need to interconvert ΔH and ΔE and you will have to deal with nonstandard values. In any situation where you must interconvert ΔH and ΔE, you should always use the standard values. In other words, your strategy map should look like this:

(heat at constant pressure) **nonstandard ΔH $\leftrightarrow$ standard ΔH $\leftrightarrow$ standard ΔE $\leftrightarrow$ nonstandard ΔE** (heat at constant volume)

You can work through the above sequence either forward or backward, and you can start and end anywhere on the map. The following examples illustrate some typical problem types.

Example 4.1.6.1

Consider the following reaction:

$$2\,CO\,(g) + O_2\,(g) \longrightarrow 2\,CO_2\,(g) \qquad \Delta E = -563.5 kJ$$

How much heat will be given off if 7.130 moles of CO reacts with excess O_2 in an open container at 25˚C?

Solution

In an open container (constant pressure), the heat equals ΔH, so we are going to need to convert ΔE into ΔH. We were given the standard value of ΔE, so we can start by using the equation $\Delta H = \Delta E + RT\Delta n_{gases}$ to calculate the standard value of ΔH. Once we know that, we can work out the nonstandard value of ΔH, which will equal the heat.

Using $\Delta H = \Delta E + RT\Delta n_{gases}$ gives us:

$$\begin{aligned} \Delta H &= -563.5 kJ + (8.314 J/mol \times K)(298.15\,K)(2\,mol – 3\,mol) \\ &= -563.5 kJ + (-2479 J) \\ &= -563.5\,kJ + (-2.479\,kJ) \\ &= -566.0\,kJ \end{aligned}$$

This is $\Delta H_{standard}$ for the reaction, corresponding to the reaction of 2 moles of CO with 1 mole of O_2. Now we calculate the nonstandard value of ΔH that corresponds to the reaction of 7.130 moles of CO.

$$\frac{-566.0\text{ kJ}}{2\text{ mol CO}} = \frac{\Delta H_{nonstandard}}{7.130\text{mol CO}}$$

Solving this equation gives $\Delta H_{nonstandard}$ = -2018 kJ, so the reaction will give off **2018 kJ of heat**.

Example 4.1.6.2

When 0.07563 mol of gaseous C_4H_{10} reacts with oxygen in a sealed, rigid container, 217.6 kJ of heat is given off. Calculate ΔH for the following reaction at 25˚C:

$$2\,C_4H_{10}\,(g) + 13\,O_2\,(g) \longrightarrow 8\,CO_2\,(g) + 10\,H_2O\,(l)$$

Solution

First, let's be sure that we understand what we're trying to calculate; the problem is asking for the standard value of ΔH for this reaction. In other words, we need to calculate the enthalpy change when 2 moles of C_4H_{10} burns.

Now, let's understand the numbers we are given. We are given the amount of heat that is produced when 0.7563 moles of C_4H_{10} burns in a rigid container. The heat is given off, so q is a negative number: $q = -217.6\,kJ$. Under these conditions, the volume is constant, so the heat equals ΔE (not ΔH). This is a nonstandard value, because we didn't use 2 moles of C_4H_{10}, so we can say that $\Delta E_{nonstandard}$ = -217.6 kJ. To convert ΔE into ΔH, we need the standard value of ΔE. Therefore, our strategy will be:

$$\text{nonstandard } \Delta E \longrightarrow \text{standard } \Delta E \longrightarrow \text{standard } \Delta H$$

We are now ready to start calculating. First, we convert the nonstandard value of ΔE into the standard value:

$$\frac{\Delta E_{standard}}{2 \text{ mol } C_4H_{10}} = \frac{-217.6\text{kJ}}{0.07563 \text{ mol } C_4H_{10}}$$

Solving this equation gives $\Delta E_{standard}$ = -5754.33 kJ

Finally, we convert the standard value of ΔE into the standard value of ΔH:

$$\begin{aligned}\Delta H &= \Delta E + RT\Delta n_{gases} \\ &= -5754.33\,kJ + (8.314\,J/mol \times K)(298.15\,K)(8\,mol–15\,mol) \\ &= -5754.33\,kJ + (-17352\,J) \\ &= -5754.33\,kJ + (-17.352\,kJ) \\ &= -5772\,kJ\end{aligned}$$

Example 4.1.6.3

When 1.500 g of MgS reacts with excess oxygen at constant pressure, 9.207 kJ of heat is given off. How much heat would be given off if the same amount of MgS reacted with oxygen at constant volume? Assume a temperature of 25˚C for both reactions. The chemical reaction is

$$MgS\,(s) + 2\,O_2\,(g) \longrightarrow MgSO_4\,(s)$$

Solution

We are given the heat at constant pressure, which equals ΔH. This is a nonstandard value, because we did not use 1 mole of MgS. Our final answer will be a nonstandard value of ΔE, since the heat equals ΔE when the volume is constant. Our strategy will be:

$$\text{nonstandard } \Delta H \longrightarrow \text{standard } \Delta H \longrightarrow \text{standard } \Delta E \longrightarrow \text{nonstandard } \Delta E$$

To begin, we convert the nonstandard ΔH value into the standard value. The molar mass of MgS is 56.37 g/mol, so 1.500 g equals 0.0266099 mol of MgS. Using our normal setup:

$$\frac{\Delta H_{standard}}{1 \text{ mol MgS}} = \frac{-9.207 \text{ kJ}}{0.0266099 \text{ mol MgS}}$$

Solving this equation gives $\Delta H_{standard} = -345.999\,kJ$.

Next, we translate our standard ΔH into the standard ΔE:

$$\begin{aligned}\Delta H &= \Delta E + RT\Delta n_{gases} \\ -345.999\,kJ &= \Delta E + (8.314\,J/mol \times K)(298.15\,K)(0\,mol–2\,mol)\end{aligned}$$

Solving this equation gives ΔE = -341.041 kJ. This is $\Delta E_{standard}$.

Finally, we calculate $\Delta E_{nonstandard}$ for the reaction of 0.0266099 moles of MgS, which will equal our heat.

$$\frac{-341.041\text{kJ}}{1 \text{ mol MgS}} = \frac{\Delta E_{nonstandard}}{0.0266099 \text{ mol MgS}}$$

Solving this equation gives $\Delta E_{nonstandard}$ = -9.075 kJ. We conclude that **the reaction gives off 9.075 kJ of heat at constant volume.**

Example 4.1.6.4

ΔH is -90 kJ the reaction

$$2\,KClO_3\,(s) \longrightarrow 2\,KCl\,(s) + 3\,O_2\,(g),$$

What are q and w when 2 moles of solid $KClO_3$ reacts at constant pressure and 25˚C? What is (ΔE) under these conditions?

Solution

The reaction is carried out at constant pressure, so q = ΔH. The problem states that we are using 2 moles of $KClO_3$, which matches the coefficient in the balanced equation, so we can use the standard value of ΔH: $q = -90\,kJ$.

To calculate w, we use the formula $w = -RT\Delta n_{gases}$:

$$w = -(8.314\,J/mol \times K)(298.15\,K)(3\,mol - 0\,mol) = -7436\,J$$

Converting to kilojoules (to be consistent with q) gives $w = -7.436\,kJ$.

To calculate ΔE, we can use our familiar relationship between ΔE and ΔH. However, it is easier to use the First Law of Thermodynamics:

$$\Delta E = q + w.$$

Substituting in the values of q and w we just calculated gives $\Delta E = -97\,kJ$. This reaction produces 97 kJ of energy, of which 90 kJ is released as heat and 7 kJ is used to do PV work.

Note that the PV work we just calculated is the standard value, corresponding to 2 moles of $KClO_3$ reacting. The next example shows how to deal with a situation where you have a nonstandard amount of reactant.

Example 4.1.6.5

If you want to get 2.000 kJ of PV work from the reaction in the previous example, how much $\mathbf{KClO_3}$ should you use?

Solution

In the previous example, we found that 7.436 kJ of PV work is done when 2 moles of $\mathbf{KClO_3}$ reacts. The PV work is proportional to the amount of reactant (just like ΔE and ΔH), so we can use the usual technique to calculate the amount of $\mathbf{KClO_3}$ here.

$$\frac{7.436\text{ kJ}}{2\text{ mol KClO}_3} = \frac{2.000\text{ kJ}}{\text{n}_{\text{nonstandard}}}$$

Solving this equation gives $n_{nonstandard}$ of **0.5379 moles of $\mathbf{KClO_3}$.**

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4.1.7: Tabulated Enthalpy Values

Tabulated ΔH Values

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature (it used too). Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH°_C) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2} + 3\,\mathrm{H_2O}(l) \quad \Delta H^\circ_{298} = -1366.8\ \mathrm{kJ} \tag{4.1.7.1}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table **4.1.7.1**. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table **4.1.7.1**: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H_c^\circ \left(\frac{\text{kJ}}{\text{mol}} \text{ at } 25^\circ\text{C}\right)$
carbon	$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$	−393.5
hydrogen	$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$	−285.8
magnesium	$\text{Mg}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{MgO}(s)$	−601.6
sulfur	$\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$	−296.8
carbon monoxide	$\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$	−283.0
methane	$\text{CH}_4(g) + 2\,\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\,\text{H}_2\text{O}(l)$	−890.8
acetylene	$\text{C}_2\text{H}_2(g) + \frac{5}{2}\text{O}_2(g) \longrightarrow 2\,\text{CO}_2(g) + \text{H}_2\text{O}(l)$	−1301.1
ethanol	$\text{C}_2\text{H}_5\text{OH}(l) + 3\,\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 3\,\text{H}_2\text{O}(l)$	−1366.8
methanol	$\text{CH}_3\text{OH}(l) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\,\text{H}_2\text{O}(l)$	−726.1
isooctane	$\text{C}_8\text{H}_{18}(l) + \frac{25}{2}\text{O}_2(g) \longrightarrow 8\,\text{CO}_2(g) + 9\,\text{H}_2\text{O}(l)$	−5461

Example 4.1.7.3: Using Enthalpy of Combustion

As Figure 4.1.7.3 suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure 4.1.7.3: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 4.1.7.1 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L C}_8\text{H}_{18}} \times \frac{1000\ \cancel{\text{mL C}_8\text{H}_{18}}}{1\ \cancel{\text{L C}_8\text{H}_{18}}} \times \frac{0.692\ \cancel{\text{g C}_8\text{H}_{18}}}{1\ \cancel{\text{mL C}_8\text{H}_{18}}} \times \frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114\ \cancel{\text{g C}_8\text{H}_{18}}} \times \frac{-5460\ \text{kJ}}{1\ \cancel{\text{mol C}_8\text{H}_{18}}} = -3.31 \times 10^4\ \text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$1.00\ \text{L}\ C_8H_{18} \longrightarrow 1.00 \times 10^3\ \text{mL}\ C_8H_{18}$$
$$1.00 \times 10^3\ \text{mL}\ C_8H_{18} \longrightarrow 692\ \text{g}\ C_8H_{18}$$
$$692\ \text{g}\ C_8H_{18} \longrightarrow 6.07\ \text{mol}\ C_8H_{18}$$
$$692\ \text{g}\ C_8H_{18} \longrightarrow -3.31 \times 10^4\ \text{kJ}$$

Exercise 4.1.7.3

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25×10^3 kJ

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure **4.1.7.4**). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



Figure **4.1.7.4**: (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure **4.1.7.5**).

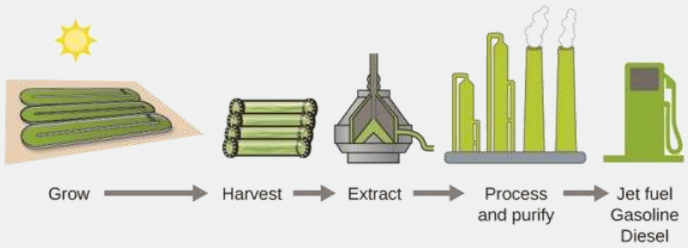


Figure **4.1.7.5**: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

A standard enthalpy of formation ΔH_f° is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is

difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = -393.5\ k\,J \tag{4.1.7.2}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $NO_{2(g)}$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = +33.2\ k\,J \tag{4.1.7.3}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Tables T1 and T2. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 4.1.7.4: Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

$$3\,O_2(g) \longrightarrow 2\,O_3(g) \quad \Delta H_{298}^\circ = +286\ k\,J$$

Solution ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $O_3(g)$ is the enthalpy change for the reaction:

$$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$$

For the formation of 2 mol of $O_3(g)$, $\Delta H_{298}^\circ = +286\ k\,J$. This ratio, $\left(\frac{286\ kJ}{2\ mol\ O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

$$\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1\ \cancel{mol\ O_3} \times \frac{286\ kJ}{2\ \cancel{mol\ O_3}} = 143\ kJ$$

Therefore, $\Delta H_f^\circ[O_3(g)] = +143\ \ k\,J/mol$.

Exercise 4.1.7.4

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, $HCl(g)$. What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $HCl(g)$ is −92.3 kJ/mol.

Answer

For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H_{298}^\circ = -184.6\ kJ$$

Example 4.1.7.5: Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

a. $C_2H_5OH_{(l)}$

b. $Ca_3(PO_4)_{2(s)}$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,C(s,\ \text{graphite}) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$
b. $3\,Ca(s) + \frac{1}{2}P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 4.1.7.5

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_{5(l)}$
b. $Na_2CO_{3(s)}$

Answer a

$$4\,C(s,\ \text{graphite}) + 5\,H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l);$$

Answer b

$$2\,Na(s) + C(s,\ \text{graphite}) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$$

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH_{298}° for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f°, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K.

Key Equations

- $\Delta E = q + w$

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

chemical thermodynamics

area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (H)

sum of a system’s internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)

heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)

work done as a system expands or contracts against external pressure

first law of thermodynamics

internal energy of a system changes due to heat flow in or out of the system or work done on or by the systemydrocarbon

compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (U)

total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH_c°)

heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH_f°)

enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state

set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function

property depending only on the state of a system, and not the path taken to reach that state

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4.1.8: Hess's Law

Hess’s Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess’s law, which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess’s law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)} \quad \Delta H = -394\ \mathrm{kJ}$$

In the two-step process, first carbon monoxide is formed:

$$\mathrm{C\,(s) + \frac{1}{2}\ O_2\,(g) \longrightarrow CO\,(g)} \quad \Delta H = -111\ \mathrm{kJ}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\mathrm{CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)} \quad \Delta H = -283\ \mathrm{kJ}$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{aligned}
&\text{Step 1: } \mathrm{C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)}\\
&\text{Step 2: } \mathrm{CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)}\\
&\overline{\text{Sum: } \mathrm{C(s) + \frac{1}{2}O_2(g) + CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + CO_2(g)}}
\end{aligned}$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$\mathrm{C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}}$$

According to Hess’s law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 4.1.8.1 to find the enthalpy change of the entire reaction from its two steps:

$$\begin{aligned}
&\mathrm{C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)} && \Delta H = -111\ \mathrm{kJ}\\
&\mathrm{CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)} && \Delta H = -283\ \mathrm{kJ}\\
&\overline{\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}} && \overline{\Delta H = -394\ \mathrm{kJ}}
\end{aligned}$$

The result is shown in Figure 4.1.8.6. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of Δ*H* values for reaction “steps” in the overall reaction) is true in general for chemical and physical processes.

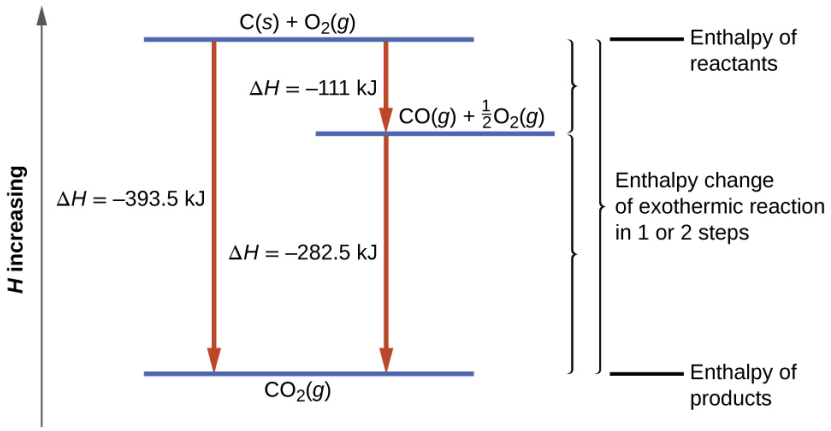


Figure **4.1.8.6**: The formation of CO_2(g) from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

$$\frac{1}{2}\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = +33.2\,\mathrm{kJ}$$

When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g) \quad \Delta H = +66.4\,\mathrm{kJ}$$

In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{HCl}(g) \quad \Delta H = -184.6\,\mathrm{kJ}$$

Then, for the "reverse" reaction, the enthalpy change is also "reversed":

$$2\,\mathrm{HCl}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \quad \Delta H = +184.6\,\mathrm{kJ}$$

Example 4.1.8.6: Stepwise Calculation of ΔH_f

Using Hess's Law Determine the enthalpy of formation, ΔH_f, of $FeCl_3$(s) from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) \quad \Delta H = -341.8\,\mathrm{kJ}$$

$$\mathrm{FeCl_2}(s) + \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H = -57.7\,\mathrm{kJ}$$

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH for the reaction:

$$\mathrm{Fe}(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) \quad \Delta H_f = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:

$$\begin{aligned}
&\mathrm{Fe}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) && \Delta H = -341.8\ \mathrm{kJ}\\
&\mathrm{FeCl_2}(s) + \tfrac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) && \Delta H = -57.7\ \mathrm{kJ}\\
\hline
&\mathrm{Fe}(s) + \tfrac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) && \Delta H = -399.5\ \mathrm{kJ}
\end{aligned}$$

The enthalpy of formation, ΔH_f, of $FeCl_3$(s) is −399.5 kJ/mol.

Exercise 4.1.8.6

Calculate ΔH for the process:

$$\mathrm{N_2}(g) + 2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g)$$

from the following information:

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta H = 180.5\ \mathrm{kJ}$$

$$\mathrm{NO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H = -57.06\ \mathrm{kJ}$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of Δ*H*) if they are difficult to determine experimentally.

Example 4.1.8.7: A More Challenging Problem

Using Hess's Law Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$\text{(i)}\ \mathrm{ClF}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{ClF_3}(g) \quad \Delta H = ?$$

Use the reactions here to determine the ΔH for reaction (i):

$$\text{(ii)}\ 2\,\mathrm{OF_2}(g) \longrightarrow \mathrm{O_2}(g) + 2\,\mathrm{F_2}(g) \quad \Delta H_{(ii)} = -49.4\ \mathrm{kJ}$$

$$\text{(iii)}\ 2\,\mathrm{ClF}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{Cl_2O}(g) + \mathrm{OF_2}(g) \quad \Delta H_{(iii)} = +205.6\ \mathrm{kJ}$$

$$\text{(iv)}\ \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \longrightarrow \tfrac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \quad \Delta H_{(iv)} = +266.7\ \mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that $\mathrm{ClF}_{(g)}$ is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$, which means that the ΔH° change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) \quad \Delta H = \frac{1}{2}(205.6) = +102.8\ k\,\mathrm{J}$$

Next, we see that $\mathrm{F_2}$ is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH changes sign and is halved:

$$\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) \quad \Delta H = +24.7\ k\,\mathrm{J}$$

To get ClF_3 as a product, reverse (iv), changing the sign of ΔH:

$$\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \quad \Delta H = -266.7\ \mathrm{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{aligned}
&\mathrm{ClF}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \tfrac{1}{2}\mathrm{Cl_2O}(g) + \tfrac{1}{2}\mathrm{OF_2}(g) && \Delta H = +102.8\ \mathrm{kJ}\\
&\tfrac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) && \Delta H = +24.7\ \mathrm{kJ}\\
&\tfrac{1}{2}\mathrm{Cl_2O}(g) + \tfrac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) && \Delta H = -266.7\ \mathrm{kJ}\\
&\overline{\mathrm{ClF}(g) + \mathrm{F_2} \longrightarrow \mathrm{ClF_3}(g)} && \overline{\Delta H = -139.2\ \mathrm{kJ}}
\end{aligned}$$

Reactants $\frac{1}{2}\mathrm{O_2}$ and $\frac{1}{2}\mathrm{O_2}$ cancel out product O_2; product $\frac{1}{2}\mathrm{Cl_2O}$ cancels reactant $\frac{1}{2}\mathrm{Cl_2O}$; and reactant $\frac{3}{2}\mathrm{OF_2}$ is cancelled by products $\frac{1}{2}\mathrm{OF_2}$ and OF_2. This leaves only reactants ClF(g) and F_2(g) and product ClF_3(g), which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH values will give the desired ΔH:

$$\Delta H = (+102.8\ \mathrm{kJ}) + (24.7\ \mathrm{kJ}) + (-266.7\ \mathrm{kJ}) = -139.2\ \mathrm{kJ}$$

Exercise 4.1.8.7

Aluminum chloride can be formed from its elements:

$$\text{(i)}\ 2\,\mathrm{Al}(s) + 3\,\mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{AlCl_3}(s) \quad \Delta H = ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\text{(ii)}\ \mathrm{HCl}(g) \longrightarrow \mathrm{HCl}(aq) \quad \Delta H_{(ii)} = -74.8\ \mathrm{kJ}$$

$$\text{(iii)}\ \mathrm{H_2}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{HCl}(g) \quad \Delta H_{(iii)} = -185\ \mathrm{kJ}$$

$$\text{(iv)}\ \mathrm{AlCl_3}(aq) \longrightarrow \mathrm{AlCl_3}(s) \quad \Delta H_{(iv)} = +323\ \mathrm{kJ/mol}$$

$$\text{(v)}\ 2\,\mathrm{Al}(s) + 6\,\mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{AlCl_3}(aq) + 3\,\mathrm{H_2}(g) \quad \Delta H_{(v)} = -1049\ \mathrm{kJ}$$

Answer

−1407 kJ

Hess's Law and Enthalpies of Formation

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H_{\text{reaction}} = \sum n \times \Delta H_f(\text{products}) - \sum n \times \Delta H_f(\text{reactants}) \tag{4.1.8.1}$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 4.1.8.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,\mathrm{NO_2}(g) + \mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{HNO_3}(aq) + \mathrm{NO}(g) \quad \Delta H = ?$$

Solution 1: Using the Equation

Alternatively, we could use the special form of Hess's law given previously:

$$\Delta H_{\text{reaction}} = \sum n \times \Delta H_f(\text{products}) - \sum n \times \Delta H_f(\text{reactants})$$

$$= \left[2 \cancel{\text{ mol HNO}_3} \times \frac{-207.4\text{ kJ}}{\cancel{\text{mol HNO}_3\,(aq)}} + 1 \cancel{\text{ mol NO}\,(g)} \times \frac{+90.2\text{ kJ}}{\cancel{\text{mol NO}\,(g)}}\right]$$
$$- \left[3 \cancel{\text{ mol NO}_2(g)} \times \frac{+33.2\text{ kJ}}{\cancel{\text{mol NO}_2\,(g)}} + 1 \cancel{\text{ mol H}_2\text{O}\,(l)} \times \frac{-285.8\text{ kJ}}{\cancel{\text{mol H}_2\text{O}\,(l)}}\right]$$
$$= 2(-207.4\text{ kJ}) + 1(+90.2\text{ kJ}) - 3(+33.2\text{ kJ}) - 1(-285.8\text{ kJ})$$
$$= -138.4\text{ kJ}$$

Solution 2: Supporting Why the General Equation Is Valid

We can write this reaction as the sum of the decompositions of $3NO_2(g)$ and $1H_2O(l)$ into their constituent elements, and the formation of 2 $HNO_3(aq)$ and 1 $NO(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH_f values for these compounds (from Tables T1 and T2), we have:

$$3\,NO_2(g) \longrightarrow \frac{3}{2}N_2(g) + 3O_2(g) \quad \Delta H_1 = -99.6\text{ kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g) \quad \Delta H_2 = +285.8\,k\,\text{J}\,[-1 \times \Delta H_f(H_2O)]$$

$$H_2(g) + N_2(g) + 3O_2(g) \longrightarrow 2\,HNO_3(aq) \quad \Delta H_3^\circ = -414.8\,kJ\,[2 \times \Delta H_f(HNO_3\ )]$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H_4 = +90.2\,k\,\text{J}\,[1 \times (NO)]$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = (-99.6\text{ kJ}) + (+285.8\text{ kJ}) + (-414.8\text{ kJ}) + (+90.2\text{ kJ})$$
$$= -138.4\text{ kJ}$$

So the standard enthalpy change for this reaction is ΔH = −138.4 kJ.

Note that this result was obtained by:

1. multiplying the ΔH_f of each product by its stoichiometric coefficient and summing those values,
2. multiplying the ΔH_f of each reactant by its stoichiometric coefficient and summing those values, and then
3. subtracting the result found in step 2 from the result found in step 1.

This is also the procedure in using the general equation, as shown.

Exercise 4.1.8.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f, is the enthalpy change accompanying the formation of 1 mole of a

substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Key Equations

- $\Delta H_{\text{reaction}} = \sum n \times \Delta H_{\text{f}}(\text{products}) - \sum n \times \Delta H_{\text{f}}(\text{reactants})$

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

chemical thermodynamics
area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (*H*)
sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)
heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)
work done as a system expands or contracts against external pressure

first law of thermodynamics
internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law
if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*)
total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH_c°)
heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH_f°)
enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state
set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function
property depending only on the state of a system, and not the path taken to reach that state

Contributors and Attributions

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SECTION OVERVIEW

Topic E- Atomic Structure

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

Electromagnetic radiation

1. Interconvert frequency and wavelength for electromagnetic radiation, and relate each of these to photon energy in J (per photon) and in kJ/mol. ($\lambda\nu = c$ and $E_{photon} = h\nu$)

Electron energy levels and atomic emission spectra

2. Recognize that electrons can only exist in certain allowed energy states.
3. Recognize that in light emission and absorption, the photon energy equals the energy difference between two electron energy states. ($E_{photon} = |\Delta E_{electron}|$)
4. Understand the measurement and meaning of ionization energy.

Special case: Bohr model (electronic structure of a one-electon atom or ion)

5. Use the Bohr energy equation to calculate the energies of the quantum levels in a hydrogen atom and in one-electron ions.
6. Calculate the energy, wavelength or frequency of light that corresponds to any electron transition in a one-electron atom or ion (using the Rydberg equation or the Bohr energy equation.)

General case: Quantum Mechanical model (modern electronic structure of an atom)

7. Understand that an energy state for a one-electron atom can be described by a wave function Ψ (atomic orbital); and describe the general shape of s, p and d orbitals.
8. Understand the relationship between atomic wave functions Ψ (atomic orbitals) and the quantum numbers n, ℓ, and m_ℓ.
9. Know and apply the rules that govern the allowed values of the quantum numbers n, ℓ, and m_ℓ.
10. Understand the physical meaning of Ψ^2 and $\Psi^2 \Delta V$.
11. Understand that one-electron wave functions (atomic orbitals) can be used to "build-up" a total wave function describing a multi-electron atom (i.e. electron configurations.)
12. Understand how orbital energy for one-electron atoms depends only on quantum number n and how orbital energy for multi-electron atoms depends on the quantum numbers n, l, and m_l.
13. Understand how the quantum number m_s describes electron spin, and the significance of the Pauli Principle and Hund's Rule in multi-electron atoms.
14. Predict the electron configurations for all of the elements in the periodic table, and identify a configuration as diamagnetic or paramagnetic.
15. Relate the electron configurations of the elements to the following properties, with a focus on the periodic nature of these properties: Ionization energy, Atomic radius, Ionic radius, Electronegativity, and Electron affinity.

5.1: Electronic Structure of Atoms

5.1.1: The Wave Nature of Light
5.1.2: The Particle Nature of Light
5.1.3: Atomic Emission Spectra and the Bohr Model
5.1.4: The Wave Behavior of Matter
5.1.5: Quantum Mechanics and Atomic Orbitals
5.1.6: 3D Representation of Orbitals
5.1.7: Many-Electron Atoms
5.1.8: Electron Configurations

5.2: Periodic Properties of the Elements

5.2.1: Development of the Periodic Table
5.2.2: Shielding and Effective Nuclear Charge
5.2.3: Sizes of Atoms and Ions
5.2.4: Ionization Energy
5.2.5: Electron Affinities
5.2.6: Metals, Nonmetals, and Metalloids
5.2.7: Group Trends for the Active Metals
5.2.8: Group Trends for Selected Nonmetals

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CHAPTER OVERVIEW

5.1: Electronic Structure of Atoms

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.

5.1.1: The Wave Nature of Light

5.1.2: The Particle Nature of Light

5.1.3: Atomic Emission Spectra and the Bohr Model

5.1.4: The Wave Behavior of Matter

5.1.5: Quantum Mechanics and Atomic Orbitals

5.1.6: 3D Representation of Orbitals

5.1.7: Many-Electron Atoms

5.1.8: Electron Configurations

Thumbnail: Electron shell diagram for Sodium, the 19th element in the periodic table of elements. (CC BY-SA; 2.5; Pumbaa)

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5.1.1: The Wave Nature of Light

Learning Objectives

- To learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves are 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 **5.1.1.1**: 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 **5.1.1.1**). 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.

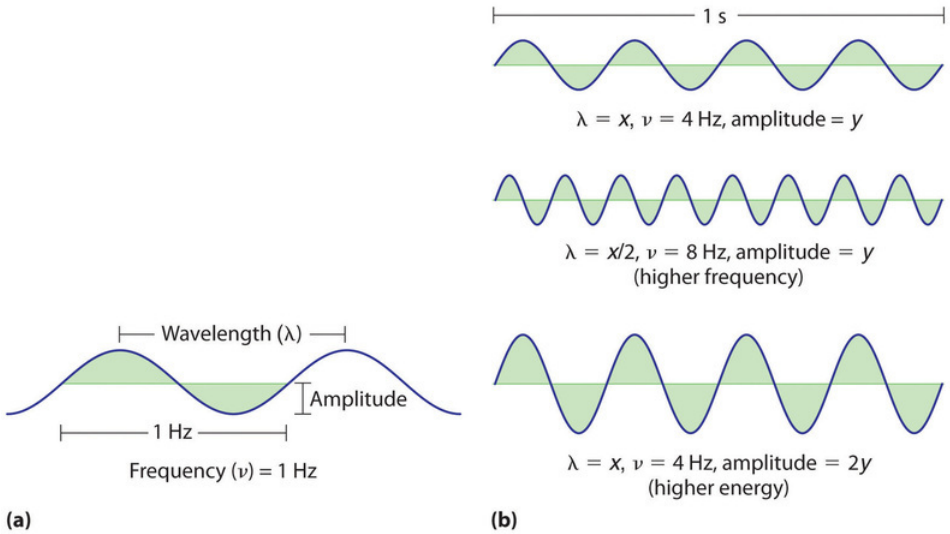


Figure **5.1.1.2**: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 5.1.1.2). As you may have noticed in Figure 5.1.1.1, 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, lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (ν, lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

The **amplitude**, 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 5.1.1.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed v, 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:

$$(\text{wavelength})(\text{frequency}) = \text{speed}$$

$$\lambda\nu = \text{v} \tag{5.1.1.1}$$

$$\left(\frac{\cancel{meters}}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{\text{second}}\right) = \frac{\text{meters}}{\text{second}} \tag{5.1.1.2}$$

> Be careful not to confuse the symbols for the speed, v (lowercase standard letter v), with the frequency, ν (lowercase Greek nu).

Different types of waves may have vastly different possible speeds and frequencies. 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**. (Figure 5.1.1.3). Some forms of electromagnetic radiation are shown in Figure 5.1.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (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.

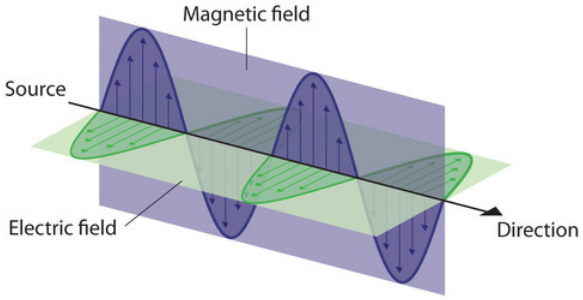


Figure 5.1.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 5.1.1.4 and Table 5.1.1.1, 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 5.1.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda\nu \tag{5.1.1.3}$$

$$\nu = \frac{c}{\lambda} \tag{5.1.1.4}$$

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.

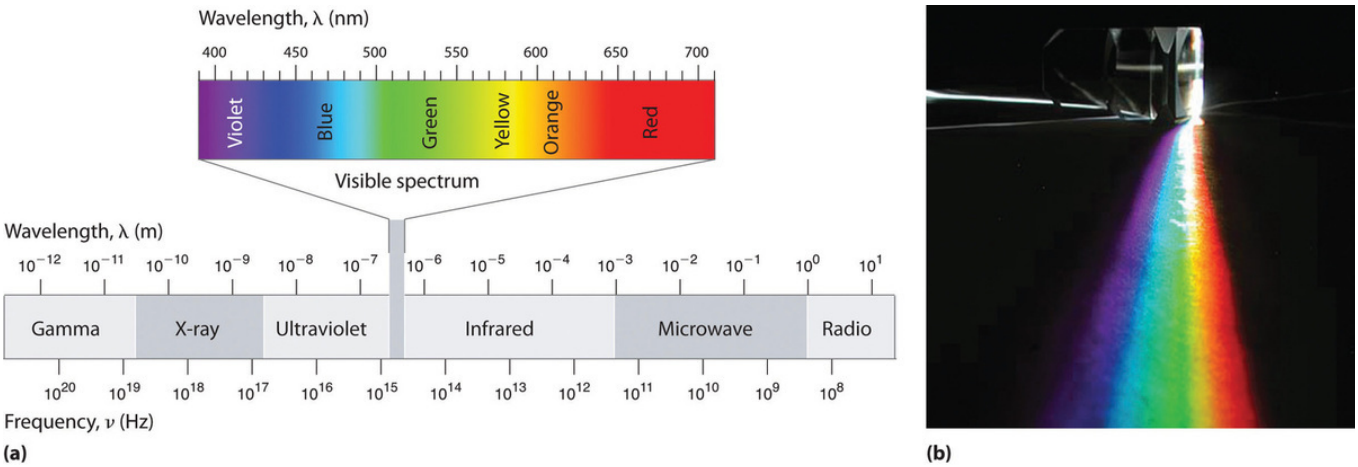


Figure 5.1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within the 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 5.1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 5.1.1.1: 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}	UV, visible
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \tag{5.1.1.5}$$

$$\propto \frac{1}{\lambda} \tag{5.1.1.6}$$

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 of the atmosphere 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 5.1.1.1: Wavelength of Radiowaves

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 5.1.1.4 to calculate the wavelength in meters.

Solution:

From Equation 5.1.1.4, 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:

$$\begin{aligned} \lambda\nu &= c \\ &= 2.998 \times 10^8 m/s \end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned} \lambda &= \frac{c}{\nu} \\ &= \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) \\ &= 2.965\ m \end{aligned}$$

Exercise 5.1.1.1

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

Summary

Understanding 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.

Contributors and Attributions

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5.1.2: The Particle Nature of Light

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 given off by a hot object. The wavelength (i.e. color) of radiant energy emitted by a blackbody 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 **5.1.2.1**: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as 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 **5.1.2.2**. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure **5.1.2.2**. Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing (in what he called "an act of despair") 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 **5.1.2.2**, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a **quantum**.

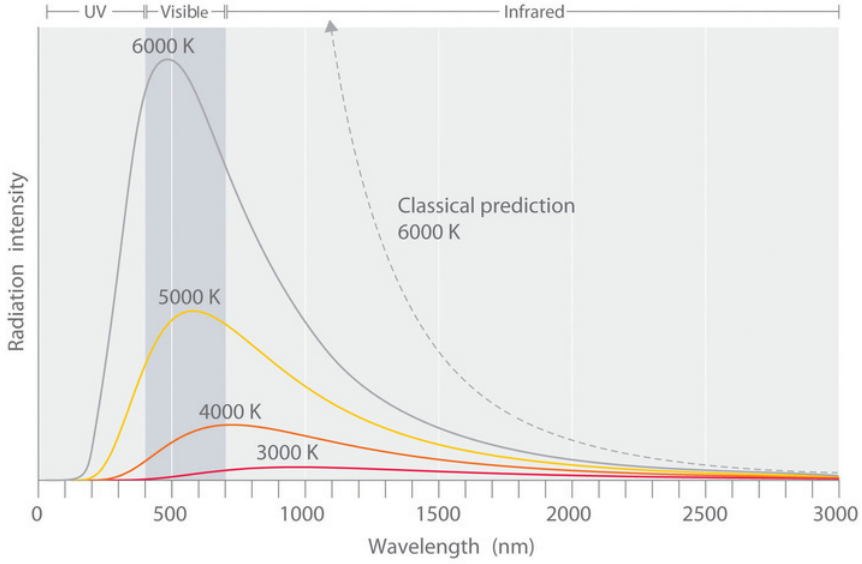
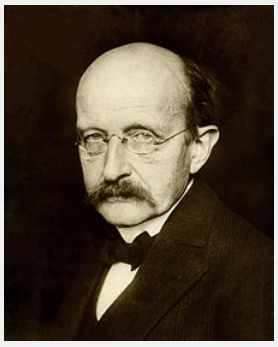


Figure **5.1.2.2**: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation it Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure **5.1.2.1** is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure **5.1.2.1**). 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(opens in new window).

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 by the equation

$$E = h\nu \tag{5.1.2.1}$$

where the proportionality constant h is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34}\ J \bullet s$$

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 **5.1.2.2**. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure **5.1.2.2**, 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 **5.1.2.3**). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

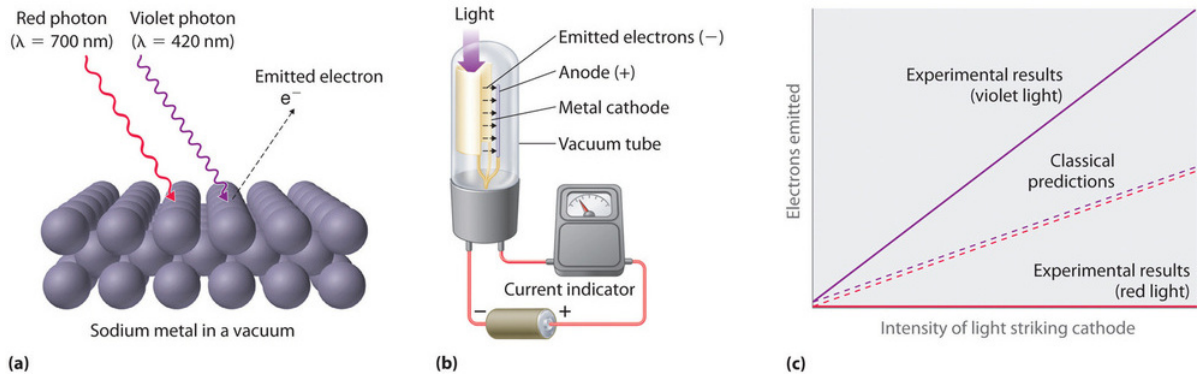


Figure **5.1.2.3**: The Photoelectric Effect (a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_o, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call **photons** (a quantum of radiant energy, each of which possesses a particular energy energy E given by Equation 5.1.2.1 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:

$$\begin{aligned} \textbf{kinetic energy of ejected electron} &= E - E_o \\ &= h\nu - h\nu_o \\ &= h\left(\nu - \nu_o\right) \end{aligned}$$

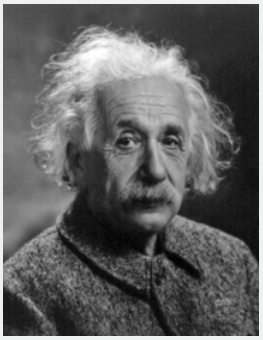
When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the *number* of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to 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. Moreover, the idea that light could behave not only as a wave but as a particle in the form of photons suggested that matter and energy might not be such unrelated phenomena after all.



Figure **5.1.2.4**: A Beam of Red Light Emitted by a Helium Neon laser reads a bar code. Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.

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 5.1.2.1

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 5.1.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 5.1.2.1 and the relationship between wavelength and frequency to calculate the energy in joules.

Solution:

The energy of a single photon is given by

$$E = h\nu = \frac{hc}{\lambda}. \tag{5.1.2.2}$$

Exercise 5.1.2.1

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

$1.287 \times 10^{-15}\ J/photon$

Answer b

4497 times

External Videos and Examples

- Calculating Energy of a Mole of Photons - Johnny Cantrell
- .Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

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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5.1.3: Atomic Emission Spectra and the Bohr Model

Learning Objectives

- To know the relationship between atomic emission spectra and the electronic structure of atoms.

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies.The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms with visible light provided this evidence.

Atomic Emission 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 of particular wavelengths, called a line spectrum, are observed rather than a continuous range of wavelengths (Figure **5.1.3.1**). 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.

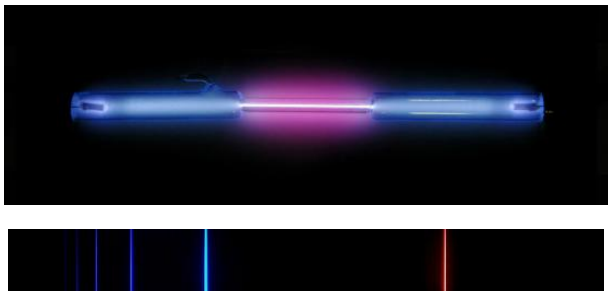


Figure **5.1.3.1**: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red/pink light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon. 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. In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

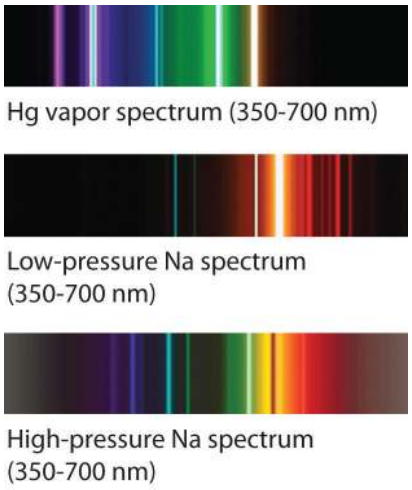


Figure **5.1.3.2**: *The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened 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.*

Such *emission spectra* were observed for many elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: 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.

The Empirical Hydrogen Equations

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. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{5.1.3.1}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and R_H the *Rydberg constant*, has a value of $1.09737 \times 10^7\ m^{-1}$ and Z is the atomic number. The Rydberg equation can be rewritten in terms of the photon energy as follows:

$$E_{photon} = R_y Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{5.1.3.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and R_y is the *Rydberg constant expressed in terms of energy* has a value of 2.180×10^{-18} J (or 1313 kJ/mol) and Z is the atomic number.

Example 5.1.3.1: The Hydrogen 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 photon energy of the lowest-energy emission in the Lyman series. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: energy of the lowest-energy Lyman emission and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into the Rydberg equation and solve for the photon energy.
B. Convert E to λ and look at an electromagnetic spectrum. Find the location corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$E_{photon} = R_y Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

A For the Lyman series, n_1 = 1. The lowest-energy line is due to a transition from the n = 2 to n = 1 orbit because they are the closest in energy. The atomic number of hydrogen is 1, so Z=1.

$$E_{photon} = (2.180 \times 10^{-18}\ J)1^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$E_{photon} = 1.635 \times 10^{-18}\ J$$

B Frequency is directly proportional to energy as shown by Planck's formula, $E = h\nu$. Wavelength is inversely proportional to frequency as shown by the formula, $\lambda\nu = c$. Using these equations, we can express wavelength, λ in terms of photon energy, E, as follows:

$$\lambda = \frac{hc}{E_{photon}}$$

$$\lambda = \frac{(6.626 \times 10^{-34}\ Js)(2.998 \times 10^{8}\ m}{1.635 \times 10^{-18}\ J}$$

$$\lambda = 1.215 \times 10^{-07}\ m = 121.5\ nm$$

Referring to the electromagnetic spectrum, we see that this wavelength is in the **ultraviolet region**.

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.

Exercise 5.1.3.1: 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

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 predicted 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.

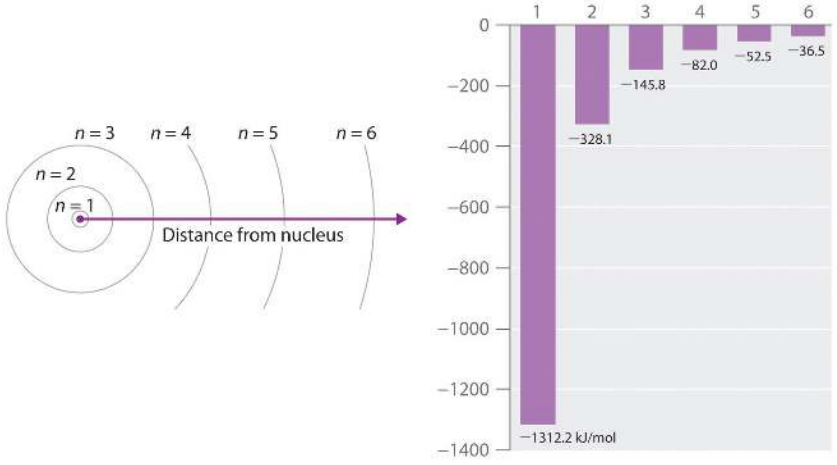
The Bohr Model for Hydrogen (and other one-electron systems)

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

$$E_n = -R_y \frac{Z^2}{n^2} \tag{5.1.3.3}$$

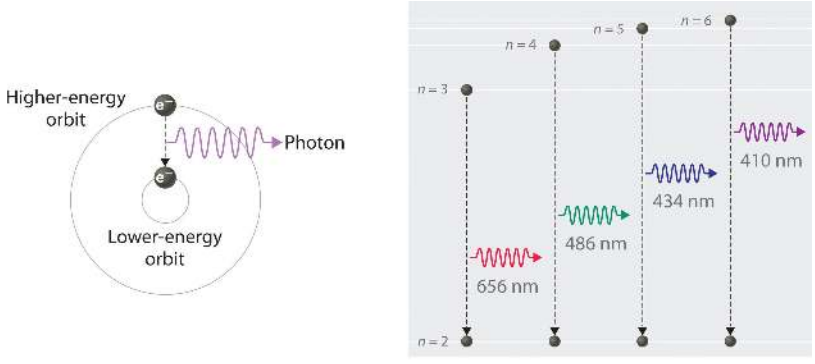
where R_y is the Rydberg constant in terms of energy, Z is the atom is the atomic number, and n is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy 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.



(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale. **(b) Hydrogen orbit energy (kJ/mol) vs. *n***

Figure **5.1.3.3**: *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.*

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 5.1.3.2 indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) 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) 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 **5.1.3.3***a*). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than 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 **5.1.3.1**).



(a) Electronic emission transition **(b) Balmer series transitions**

Figure **5.1.3.4**: *The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with n ≥ 3 to the orbit with n = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.*

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_{final}} - E_{n_{initial}}$ where n_{final} is the final orbit and n_{initial} is the initial orbit. Substituting from Bohr's energy equation (Equation 7.3.3) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = \left(-\frac{Z^2 R_y}{n^2_{final}}\right) - \left(-\frac{Z^2 R_y}{n^2_{initial}}\right) \tag{5.1.3.4}$$

$$\Delta E = -R_y Z^2 \left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}}\right) \tag{5.1.3.5}$$

If we distribute the negative sign, the equation simplifies to

$$\Delta E = R_y Z^2 \left(\frac{1}{n^2_{initial}} - \frac{1}{n^2_{final}}\right) \tag{5.1.3.6}$$

If $n_{initial} > n_{final}$, then 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 **5.1.3.3** and $\Delta E_{electron}$ will be a negative value, reflecting the decrease in electron energy. Note that this is essentially the same equation 7.3.2 that Rydberg obtained experimentally. Bohr calculated the value of R_y from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of 2.180×10^{-18} J, the same number Rydberg had obtained by analyzing the emission spectra. The only significant difference between Bohr's theoretically derived equation and Rydberg's experimentally derived equation is a matter of sign. Rydberg's equation always results in a positive value (which is good since photon energies are always positive quantities!!), whereas Bohr's equation can be either negative (the electron is decreasing in energy) or positive (the electron is increasing in energy). Regardless, the energy of the emitted photon corresponds to the change in energy of the electron.

$$E_{photon-emitted} = |\Delta E_{electron}| \tag{5.1.3.7}$$

We can now understand the theoretical basis for the emission spectrum of hydrogen (**5.1.3.3*b***); the lines in the visible series of emissions (the Balmer 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 (Figure **5.1.3.3*a***). 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 (Figure **5.1.3.1*a***). 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 **5.1.3.4**

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File:Hydrogen_transitions.svg

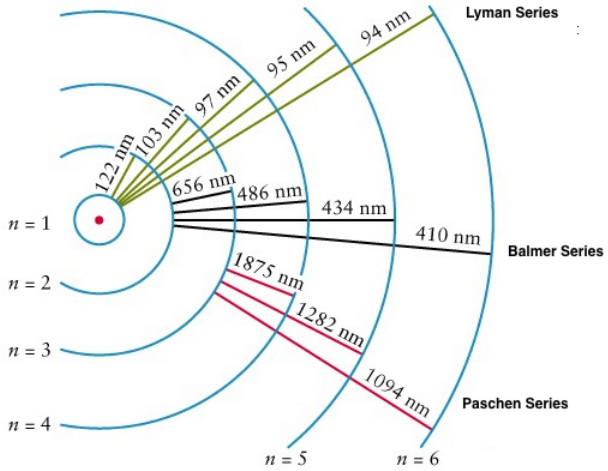


Figure **5.1.3.5**: *Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding 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. The Backett and Pfund series not shown. (Energy levels are not to scale.)*

Using Atoms to Time

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.

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 exists at only certain distances from the nucleus, 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 **5.1.3.5**). In fact, Bohr's model worked only for species that contained just one electron: H, He^{+}, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

Absorption Spectra

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum. The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum.

> 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.

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.

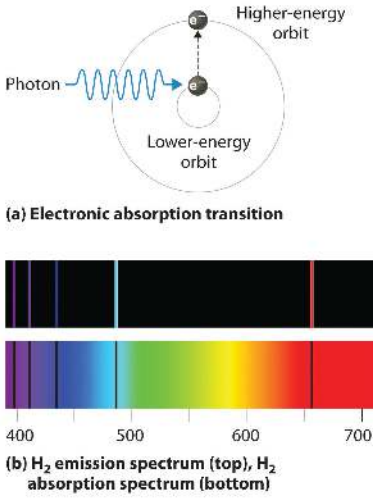


Figure **5.1.3.6**: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. Note that these images also include a 5th line, appearing slightly below 400 nm. This line corresponds to electron transitions between n = 2 and n = 7 and exceeds the commonly visible range of light.

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 **5.1.3.7** Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

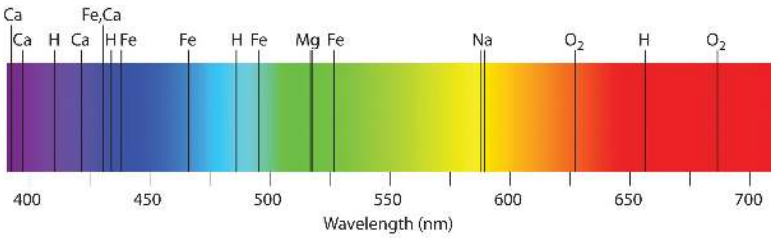


Figure **5.1.3.7**: *The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.*

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. 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. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

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5.1.4: The Wave Behavior of Matter

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 famous equation:

$$E = mc^2 \tag{5.1.4.1}$$

According to this theory, a photon of energy $E = h\nu = \dfrac{hc}{\lambda}$ has a nonzero mass, which can be solved for as follows:

$$E = mc^2$$

$$\frac{hc}{\lambda} = mc^2$$

$$m = \frac{h}{\lambda c} \tag{5.1.4.2}$$

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

$$\lambda = \frac{h}{m\mathrm{v}} \tag{5.1.4.3}$$

where

- h is Planck's constant,
- m is the mass of the particle, and
- v is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example **5.1.4.1**, 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 5.1.4.1: Wavelength of a Baseball in Motion

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 5.1.4.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that m = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 44.69\ m/s$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^2 \cdot \cancel{s}^{-2} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s}^{-1}\right)} = 9.95 \times 10^{-35}\ m$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

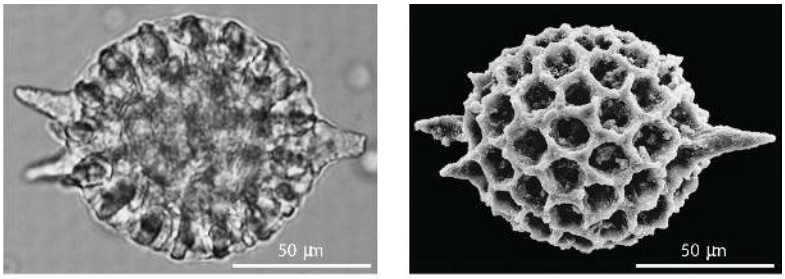
Exercise 5.1.4.1: Wavelength of a Neutron in Motion

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 5.1.4.1, 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, however, 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 5.1.4.1).



(a) Radiolarian under light microscope (b) Radiolarian under electron microscope

Figure 5.1.4.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

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. 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. An "uncertainty principle" for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit wavelike characteristics will also undergo diffraction from slits whose size is on 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** 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:

$$(\Delta x)\,(\Delta\,[mv]) \geq \frac{h}{4\pi} \tag{5.1.4.4}$$

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:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{5.1.4.5}$$

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 5.1.4.4, 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 5.1.4.2: Quantum Nature of Baseballs

Calculate the minimum uncertainty in the position of the pitched baseball from Example 5.1.4.1 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 5.1.4.4) 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 (Equation 5.1.4.4) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi \tag{5.1.4.6}$$

. 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

$$\Delta v = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s \tag{5.1.4.7}$$

C Therefore,

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right) \tag{5.1.4.8}$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\,(\cancel{s^2})}\right)\left(\frac{1\ \cancel{s}}{(0.149\ \cancel{kg})\,(0.4469\ \cancel{m})}\right) \tag{5.1.4.9}$$

$$\Delta x \geq 7.92 \pm \times 10^{-34}\ m \tag{5.1.4.10}$$

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 5.1.4.2

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)

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 5.1.4.2). If the length of the string is L, then the lowest-energy vibration (the fundamental) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L$$

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

$$\lambda = \frac{2L}{n} \tag{5.1.4.11}$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure 5.1.4.2 that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

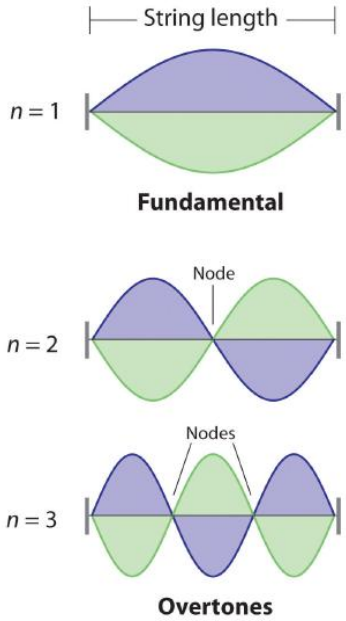


Figure 5.1.4.2: Standing Waves on a Vibrating String. The vibration with \(n = 1\) is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain \(n − 1\) nodes.

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

$$2\pi r = n\lambda \tag{5.1.4.12}$$

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 5.1.4.3). 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 nonresonant 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 5.1.4.12, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

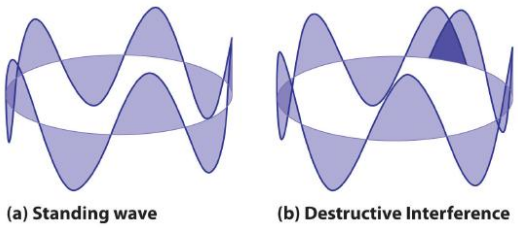


Figure 5.1.4.3: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with \(n = 5\), the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference 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.

Like 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. 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 now 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.

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.

$$\lambda = \frac{h}{mv}$$

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.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

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.

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5.1.5: Quantum Mechanics and Atomic Orbitals

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.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger's equations.

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 three spatial 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* -*or*- Spherical coordinates (r, θ, φ)), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying 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 6.5.1).

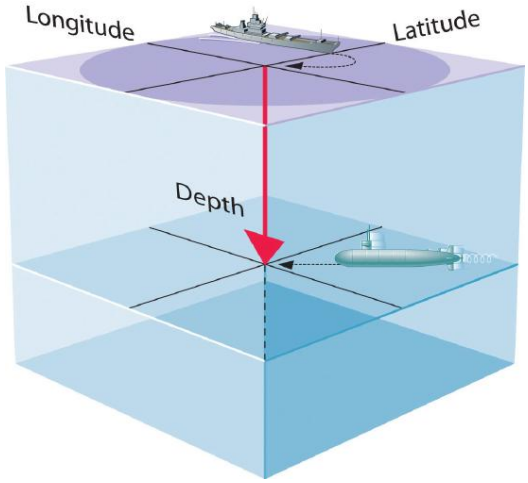


***Figure* 5.1.5.1**: *The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object*

For electrons, we will be using standing waves, which do not vary with time, to describe the position of an electron. Spherical coordinates (r, θ *and* ϕ) are commonly used when describing the position of an electron within an atom. We will

often focus only on the radial component of the wave function! Note that the value of the r-coordinate tells us the distance of the electron from the nucleus (at r=0).

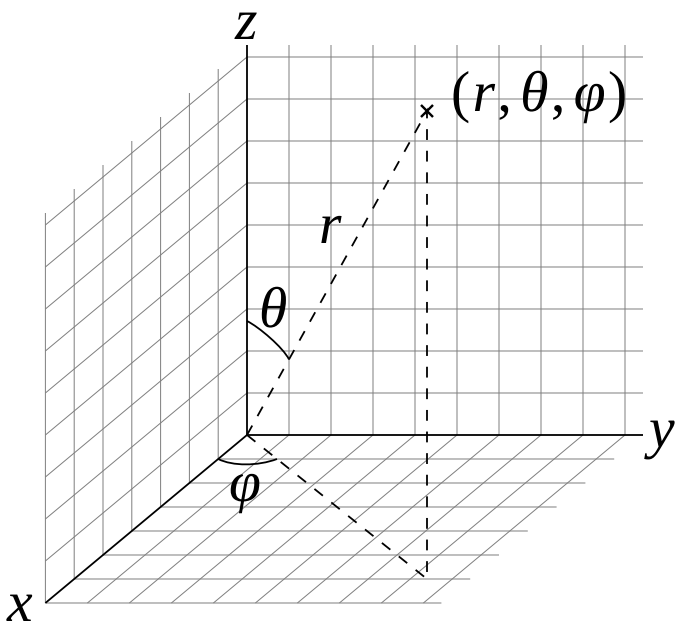


Figure* 5.1.5.2:* Spherical coordinates (*r*, *θ*, *φ*) as commonly used to locate an electron within an atom: radial distance *r*, polar angle *θ* (theta), and azimuthal angle *φ* (phi). (The symbol *ρ* (rho) is often used instead of *r*.) Andeggs, Public domain, via Wikimedia Commons

- **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 $\sqrt{-1}^2 = -1$] and 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 5.1.5.2.
- **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 previously, 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 cancelation 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.

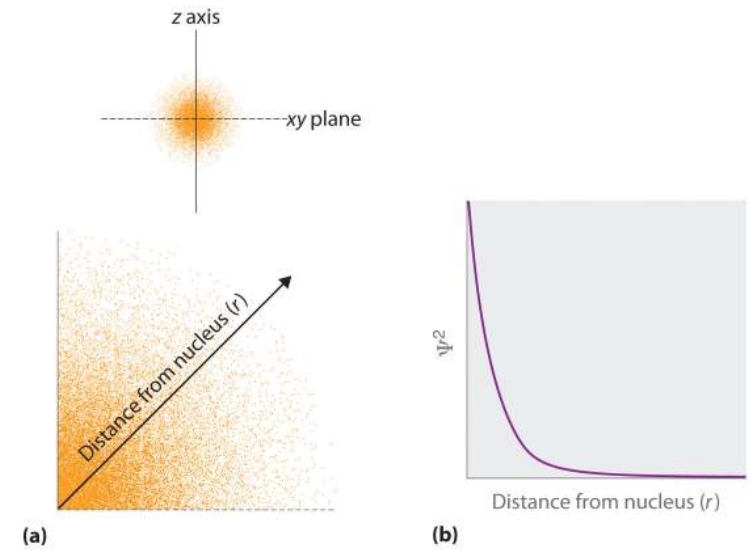


Figure **5.1.5.3**: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest 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.

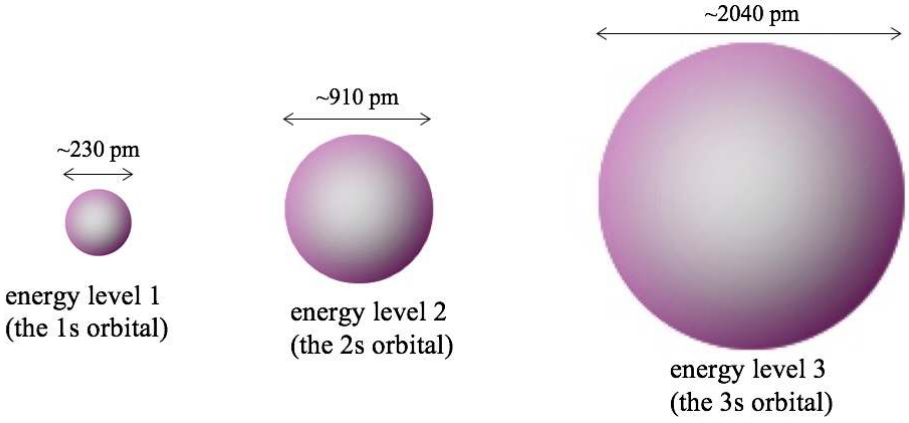
Atomic Orbitals

You've probably seen the term "orbital" in previous chemistry classes. An orbital is a distribution for an electron. In other words, "an orbital" means "a map of where the electron tends to spend its time." This map is provided by the wave function (Ψ), so "orbital" and "wave function" mean the same thing (more or less).

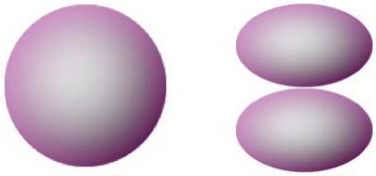
Visualizing an orbital can be tricky, because electrons can be just about anywhere. The electron in a hydrogen atom could be one foot away from the nucleus. However, this is *extremely* unlikely; the probability of the electron being that far away is around $10^{-2,502,324,325}$. Electrons spend the vast majority of their time close to the nucleus. To depict an orbital, then, we can draw a picture of the region in which the electron spends 90% of its time; this is called the **90% contour**.

We can only calculate wave functions for atoms with one electron, so we can only draw pictures of orbitals for one-electron atoms. When we do this for hydrogen, we notice a few things right away….

1) Orbitals that have different **energies** are always different **sizes**. For example, here are the 90% contours of the simplest-looking orbitals for energy levels 1, 2 and 3 in a hydrogen atom, along with the diameters of the 90% contours.



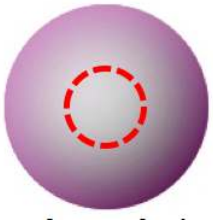
2) Some orbitals have the same energy, but are different **shapes**. For example, here are the 90% contours of two orbitals that have the same energy. Note that although their shapes are different, they are roughly the same size, because they have the same energy.



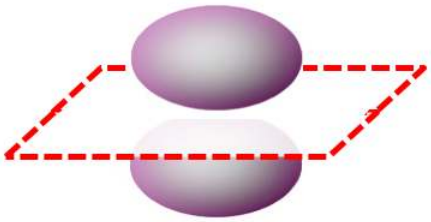
the 2s orbital (energy level 2) | the $2p_z$ orbital (energy level 2)

3) Most orbitals have at least one **nodal surface**. A nodal surface is a plane or a sphere on which the electron can never be found; the probability of the electron appearing on the nodal surface is zero. Nodal surfaces are directly connected with the energy of an orbital. **The higher the energy of the orbital, the larger the number of nodal surfaces**.

A spherical nodal surface is called a **radial node**, because you can describe it completely by telling what its radius is. When an orbital has a radial node, the electron can be inside the sphere, or outside the sphere, but never on the sphere. For example, the 2s orbital has a radial node, which is shown as a red dashed circle in the picture below. The electron spends about 5% of its time inside the red circle (actually a sphere) and 95% of its time outside the circle.



A planar nodal surface is called an **angular node**, because you can describe it by telling what angle it makes with one of the Cartesian axes. When an orbital has an angular node, the electron can be on either side of the plane, but never on it. For example, the $2p_z$ orbital has an angular node (a horizontal plane), as shown below. The plane extends infinitely far in all directions.



Orbitals can have more than one nodal surface. For example, the $3p_z$ orbital has two nodal surfaces: a radial node (a sphere) and an angular node (a plane).

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wavefunction. You can think of them as a sort of shorthand notation for the wavefunction. 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.

The Principal Quantum Number

The **principal quantum number** (n) gives us a great deal of information about an orbital. It tells us…

- …the **energy** of the orbital
- …the relative **size** of the orbital (larger n = larger orbital)
- …the **number of nodal surfaces** that the orbital has (it's always **n – 1**)

The name of any orbital always starts with the value of n. For a 1s orbital, n = 1, and for a 2p orbital, n = 2. The principal quantum number also tells us how many different orbitals (wave functions) have a particular energy. **For any energy level, the total number of orbitals is n^2**. For example, there are four different orbitals that have n = 2 (because $2^2 = 4$) and nine different orbitals that have n = 3 (because $3^2 = 9$).

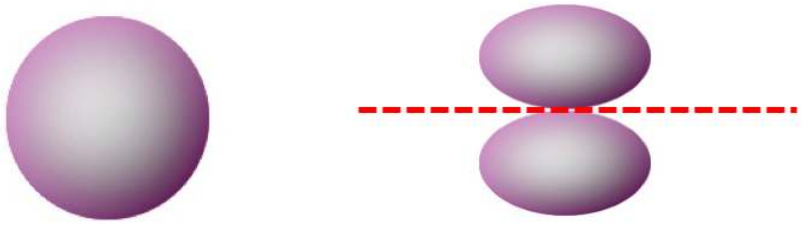
There is no limit on the size of n; it can be any number from 1 to infinity. As n gets larger, the energy of the orbital gets larger (closer to zero) and the electron gets farther from the nucleus on average. When the energy reaches zero, the electron is completely removed from the atom.

$$n = 1, 2, 3, 4, \ldots \tag{5.1.5.1}$$

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 and energies. 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 azimuthal quantum number tells us the general shape of an orbital. Specifically, it tells us **the number of angular nodes** that the orbital has. The angular nodes create the shape of an orbital. For instance, look at the difference between a 2s orbital (no angular nodes) and a 2p orbital (one angular node). Both orbitals have one nodal surface, but the 2s orbital has a radial node (a sphere), which is hidden inside the 90% contour, whereas the 2p orbital has an angular node, which chops the orbital into two pieces.



The value of l is always part of the orbital's name, but it is "coded" in the following fashion:

If l = 0, we have an **s orbital** (1s, 2s, 3s, 4s, 5s…)

If l = 1, we have a **p orbital** (2p, 3p, 4p, 5p…)

If l = 2, we have a **d orbital** (3d, 4d, 5d…)

If l = 3, we have an **f orbital** (4f, 5f…)

The value of l also tells us how many orbitals of that type there are. **If we specify both n and l, the total number of orbitals is 2l + 1**. For example, there are five different 3d orbitals, because l = 2 for any kind of d orbital, and (2 × 2) + 1 = 5. The value of n doesn't matter; there are also five different 4d orbitals, five different 5d orbitals, etc.

The value of l is limited by the value of n, because the number of angular nodes can't be larger than the total number of nodes (which is n – 1). Therefore, **l is always smaller than n**. The allowed values of *l* depend on the value of *n* and can range from 0 to *n* − 1:

$$l = 0, 1, 2, \ldots, n - 1 \tag{5.1.5.2}$$

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.

Example 5.1.5.1: Interpreting *n* and *l*

Here are some sample questions to illustrate the concepts we've looked at so far.

If n = 4, what are the possible values of l?

l *can be 0, 1, 2 or 3.*

What are the names of each of the orbitals that correspond to these combinations of n and l?

4s orbital (n = 4, l *= 0), 4p orbital (n = 4,* l *= 1), 4d orbital (n = 4,* l *= 2), and 4f orbital (n = 4,* l *= 3).*

How many nodes does each of these orbitals have? How many of them are angular and how many are radial?

All of these orbitals have 3 nodes, because the number of nodes equals n – 1, and n is 4 for all of these orbitals.

· *The 4s orbital has* l *= 0, so it has no angular nodes. We already know that it has three nodes, so it must have three radial nodes.*

· *The 4p orbital has* l *= 1, so it has one angular node. Therefore, it must have two radial nodes.*

· *The 4d orbital has* l *= 2, so it has two angular nodes. Therefore, it must have one radial node.*

· *The 4f orbital has* l *= 3, so it has three angular nodes. Therefore, it has no radial nodes.*

What is the energy of each of these orbitals?

These are hydrogen orbitals, so we can use the Bohr formula to calculate their energy. We know that all of them have n = 4, and the atomic number Z is 1 for hydrogen, so we have:

$$E = (-1313\ kJ/mol)\left(\frac{1^2}{4^2}\right) = \mathbf{-82.06\ kJ/mol}$$

Note that all four of these orbitals have the same energy.

Rank these orbitals in order of size.

They are all approximately the same size, because they have the same value of n.

If an orbital has n = 7 and* l *= 2, what type of orbital is it?

It is a 7d orbital.

How many nodes does this orbital have? How many of them are radial nodes?

This orbital has six nodes, because the number of nodes equals n – 1, and 7 – 1 = 6. To find the number of radial nodes, we must find the number of angular nodes. The number of angular nodes always equals l*, so this orbital has 2 angular nodes. Therefore, it has 6 – 2 = 4 radial nodes.*

A hydrogen orbital has one angular node and four radial nodes. What kind of orbital is it?

This is a 6p orbital. It has one angular node, so l *= 1, making it a p orbital. The total number of nodes is 1 + 4= 5, and this must equal n – 1, so n = 6 for this orbital.*

A hydrogen orbital has five radial nodes, and its energy is -16.21 kJ/mol. What type of orbital is it?

We can calculate the value of n for this orbital, because we know its energy:

$$E = (-1313\ kJ/mol)\left(\frac{l^2}{n^2}\right) = -16.21\ kJ/mol$$

Solving for n gives n = 8.999965…, which we round to 9, since n must be a whole number. Next, we figure out the value of l*. Since n = 9, this orbital has 8 nodes. We're told that five of them are radial nodes, so the orbital has 8 – 5 = 3 angular nodes. Therefore, n = 9 and* l *= 3 for this orbital, making it a 9f orbital.*

How many orbitals have n = 4?

There are 16 orbitals that have n = 4. The total number of orbitals that have a given value of n is n^2*;* $4^2 = 16$.

How many orbitals have n = 5 and* l *= 3?

There are 7 orbitals that have this combination of n and l*. The number of orbitals that have a specific combination of n and* l *is* $2l + 1$*;* $(2 \times 3) + 1 = 7$.

How many orbitals have n = 5 and* l *= 5?

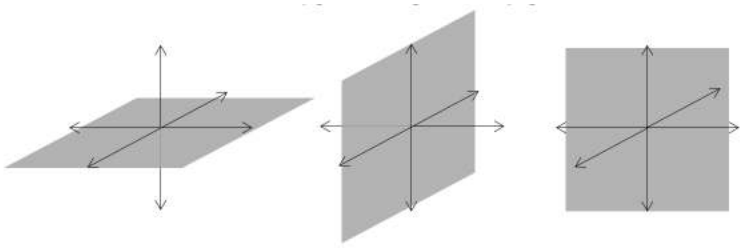
No orbitals have this combination. l *must always be smaller than n, because the total number of nodes is n – 1 and the number of angular nodes is* l*. Therefore, the largest possible value of* l *is n – 1.*

How many 6s orbitals are there?

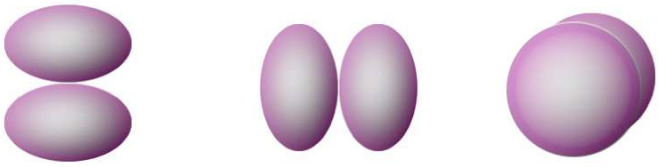
There is just one 6s orbital. For 6s orbitals, n = 6 and l *= 0. The number of orbitals that has this combination of n and* l *is* $2l + 1 = (2 \times 0) + 1 = 1$.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The magnetic quantum number tells us the **orientation** of an orbital respect to an applied magnetic field.. More specifically, it tells us the orientation of the angular nodes. For example, a 2p orbital has one angular node, but that node can have three orientations: the *xy* plane, the *xz* plane, or the *yz* plane:



As a result, there are three different 2p orbitals, each oriented along one of the Cartesian axes.



The $2p_z$ orbital (oriented along the z axis, with its node in the xy plane)

The $2p_x$ orbital (oriented along the x axis, with its node in the yz plane)

The $2p_y$ orbital (oriented along the y axis, with its node in the xz plane)

The value of m_l determines the orientation of the orbital, essentially by determining how far the orbital is from the z axis. If the orbital is aligned along the z axis, m_l is zero. For the other orbitals, m_l is ±1; one of the orbitals has m_l = -1 and the other has m_l = 1. There is no fixed rule for this assignment though.

The possible values for m_l are controlled by the value of l. **For a given value of l, m_l can be any integer from –l to +l.** The allowed values of m_l therefore depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{5.1.5.3}$$

For example, if l is 2 (i.e. if we are talking about d orbitals), m_l can be -2, -1, 0, 1, or 2. The number of options for m_l must match the total number of orbitals, which is 2l + 1; note that in this case, 2l + 1 = 5, and there are indeed five options for the value of m_l.

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 5.1.5.2: 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 = 16

Exercise 5.1.5.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with n = 3?

Answer

three subshells; nine orbitals

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 7.5.1):

- Each principal shell has *n* subshells. For *n* = 1, only a single subshell is possible (1*s*); for *n* = 2, there are two subshells (2*s* and 2*p*); for *n* = 3, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with *n* ≥ 2 also has an *np* subshell, and any shell with *n* ≥ 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 2*l* + 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.

Table **5.1.5.1**: 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	

Example5.1.5.2: The Three Quantum Numbers

Here are some sample questions that look at all three quantum numbers we've examined so far: n, l, and m_l.

What are the possible values of n, l, and m_l for a 13f orbital?

The name of the orbital tells us that n is 13 and l *is 3. (Remember the "*l *code": s, p, d, f corresponds to* l *= 0, 1, 2, 3.) Since* l *is 3, m_l can be any integer from -3 to +3, so the possible values of m_l are -3, -2, -1, 0, 1, 2 and 3.*

An orbital has n = 4, l = 2, and m_l = -2. What kind of orbital is this?

This is a 4d orbital. The value of m_l tells us about the orientation of the orbital, but I don't expect you to know which orbital corresponds to which value of m_l, so you can ignore m_l when you're naming orbitals.

How many different orbitals have n = 6, l = 1, and m_l = 1?

Just one orbital has this combination. When you specify the values of all three quantum numbers, you have specified a single orbital.

How many different orbitals have n = 6 and m_l = 1?

This is a trickier question, because the question didn't specify the value of l. *We must consider all of the possible values of* l *that are compatible with* $n = 6$ *and* $m_l = 1$…

$n = 6$, l = 0, $m_l = 1$ *impossible,* m_l *can't be larger than* l

$n = 6$, l = 1, $m_l = 1$ *okay – this is a 6p orbital*

$n = 6$, l = 2, $m_l = 1$ *okay – this is a 6d orbital*

$n = 6$, l = 3, $m_l = 1$ *okay – this is a 6f orbital*

$n = 6$, l = 4, $m_l = 1$ *okay – this is a 6g orbital (but you don't need to know that)*

$n = 6$, l = 5, $m_l = 1$ *okay – this is a 6h orbital (but you don't need to know that)*

$n = 6$, l = 6, $m_l = 1$ *impossible,* l *must be smaller than* n

l *larger than 6 impossible,* l *must be smaller than* n

Counting up the acceptable combinations, we see that there are five orbitals that have $n = 6$ *and* $m_l = 1$.

***How many different orbitals have* l = 3 *and* m_l = -2?**

Infinite orbitals have this combination, because we didn't specify the value of n. We know that n must be larger than l, *but that just means that n can't be 1, 2 or 3; it can still be any number from 4 to infinity. We could have a 4f orbital (*$n = 4$, l = 3*), a 5f orbital (*$n = 5$, l = 3*), a 6f orbital (*$n = 6$, l = 3*), etc. etc.*

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 spatial variables (Cartesian coordinates: x, y, and z *-or-* Spherical coordinates (r, θ, φ) *)* 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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5.1.6: 3D Representation of Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of containing an electron.

One way of representing electron probability distributions was illustrated previously for the 1*s* orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is very small but *not* zero.

In contrast, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure **5.1.6.1***a*), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (Figure **5.1.6.1***b*), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure **5.1.6.1**. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure **5.1.6.1***c*). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure **5.1.6.1***d*). Most important, when r is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure **5.1.6.1***d*).

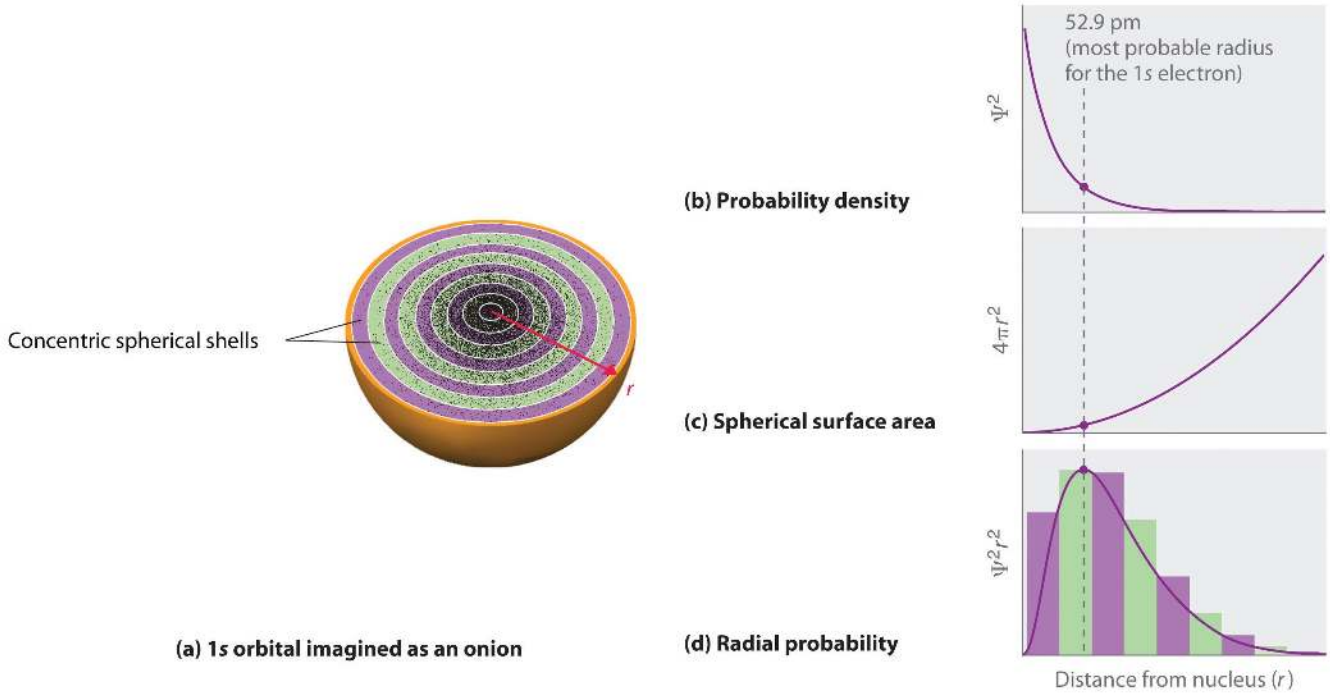


Figure* 5.1.6.1: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a*

given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the n = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure **5.1.6.2** compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (Figure **5.1.6.2***c*). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave *phase* in the wavefunction Ψ.

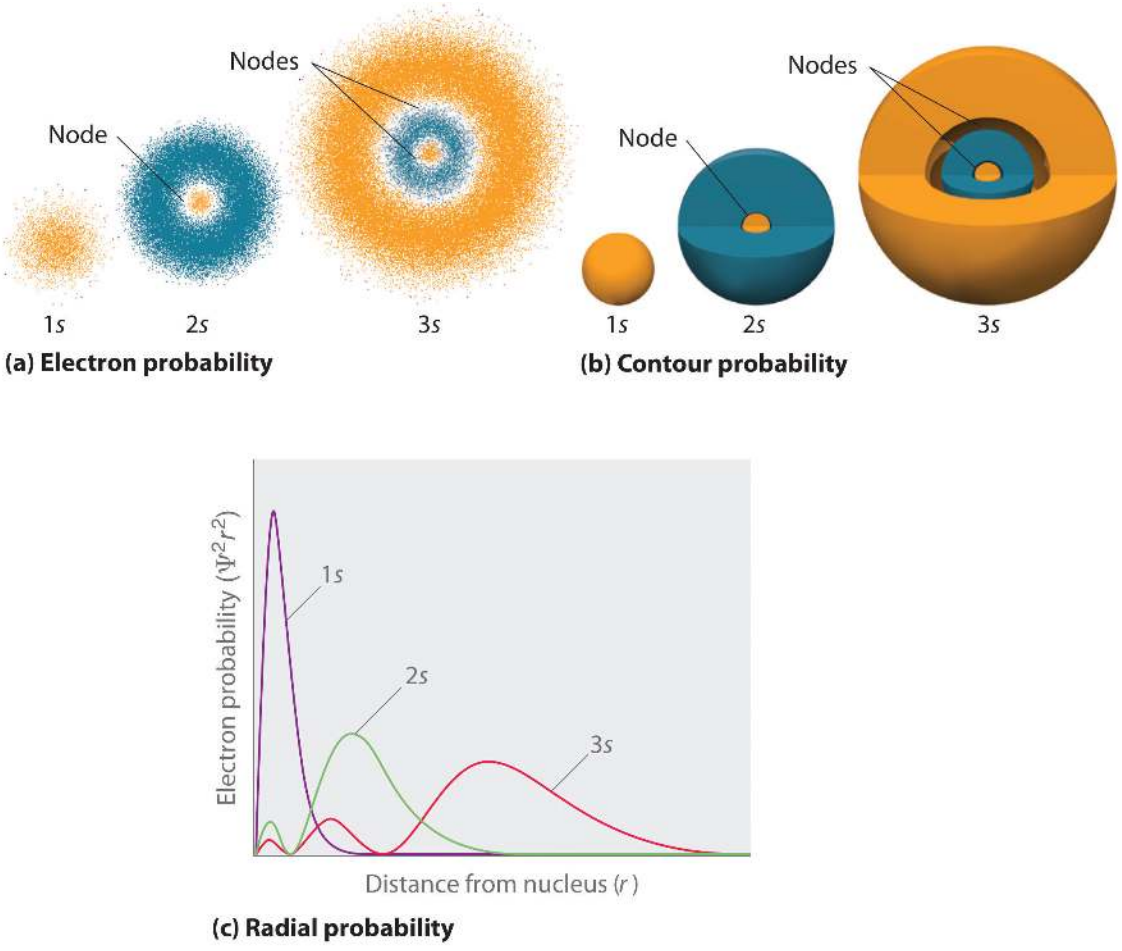


Figure* 5.1.6.2: Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r.*

s Orbitals (l=0)

Three things happen to *s* orbitals as *n* increases (Figure **5.1.6.2**):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure **5.1.6.2**. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals.

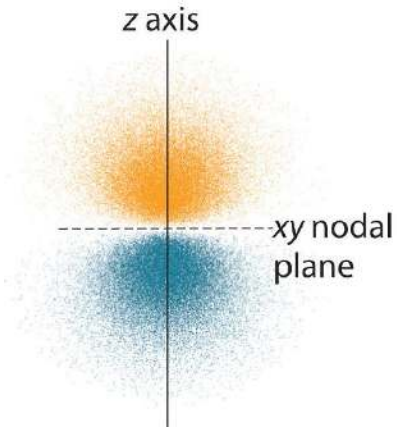


Figure **5.1.6.3**: Electron Probability Distribution for a Hydrogen 2*p* Orbital. The nodal plane of zero electron density separates the two lobes of the 2*p* orbital. As in Figure **5.1.6.2**, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure **5.1.6.3**. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure **5.1.6.4**, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each *p* orbital has just one **angular node.** The angular node has the shape of plane in the following illustrations. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

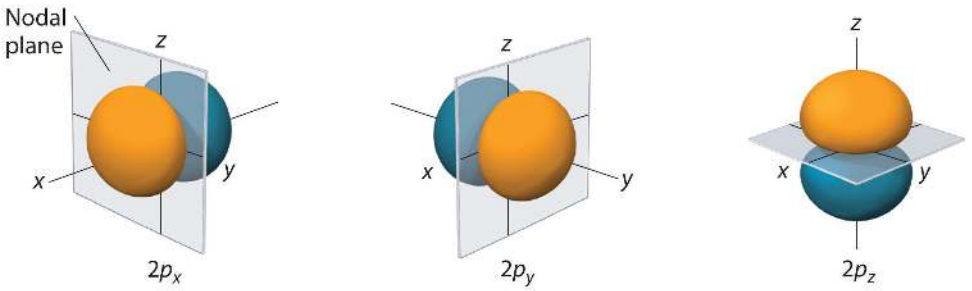


Figure 5.1.6.4 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative. Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure **5.1.6.4**.

d Orbitals (l=2)

Subshells with $l = 2$ have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to $n = 3$. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2.

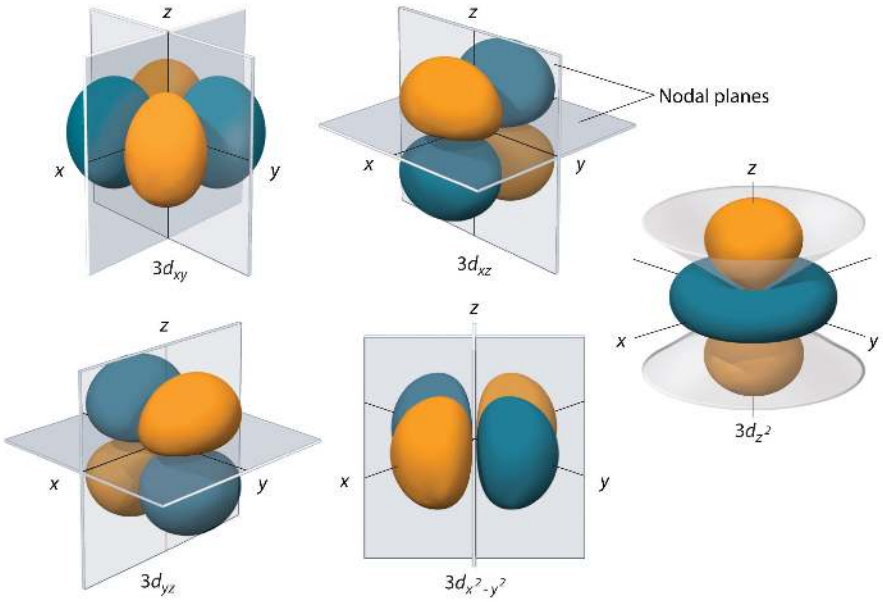


Figure **5.1.6.5**: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $\mathbf{3d_{z^2}}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals, shown in Figure **5.1.6.5**, have more complex shapes than the 2p orbitals. All five 3d orbitals contain **two angular nodes**. The angular nodes have the shape of a planar or conical surface where there is zero probability of finding the electron. Note the contrast as compared to one angular node for each p orbital and zero angular nodes for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $\mathbf{3d_{xy}}$, $\mathbf{3d_{xz}}$, and $\mathbf{3d_{yz}}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $\mathbf{3d_{x^2-y^2}}$ orbital. The fifth 3d orbital, called the $\mathbf{3d_{z^2}}$ orbital, has a unique shape: it looks like a $\mathbf{2p_z}$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $\mathbf{3d_{z^2}}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure **5.1.6.5**, the phase of the wave function is positive for the two lobes of the $\mathbf{dz^2}$ orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure **5.1.6.5**.

f Orbitals (l=3)

Principal shells with $n = 4$ can have subshells with $l = 3$ and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three angular nodes, so their shapes are complex. Because *f* orbitals are not particularly important

for our purposes, we do not discuss them further, and orbitals with higher values of l are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure **5.1.6.6**; note that the orbital energies depend on *only* the principal quantum number n. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of n (e.g., the three 2*p* orbitals) are **degenerate**, meaning that they have the same energy. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure **5.1.6.6** shows that the energy levels become closer and closer together as the value of n increases, as expected because of the $1/n^2$ dependence of orbital energies.

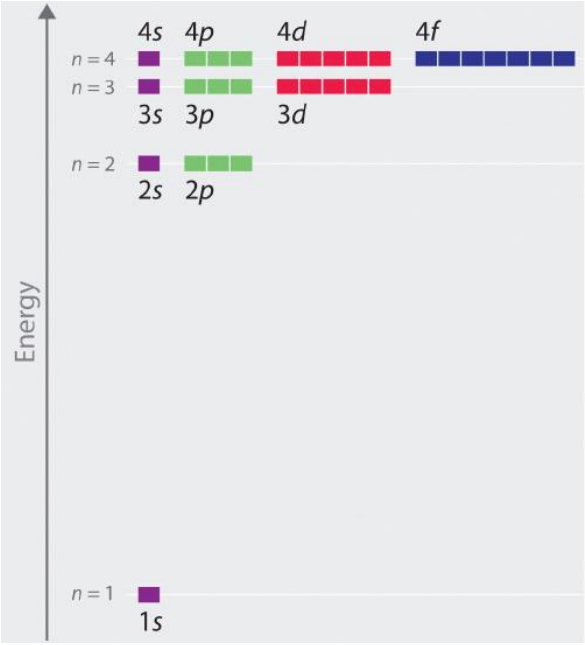


Figure **5.1.6.6**: Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2}Rhc \tag{5.1.6.1}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of $\ell = 0$, 1, 2, and 3. Orbitals with $\ell = 0$ are s orbitals and they are spherically symmetrical with no angular nodes. The s orbitals have the greatest electron density occurring at the nucleus. Orbitals with $\ell = 1$ are p orbitals and contain a angular node (a nodal surface shaped like a plane) that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with two angular nodes (nodal surfaces shaped like planes or cones). Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Three things happen to all orbital types (s, p, d, f) as *n* increases:

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. They become higher in energy as *n* increases.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Contributors and Attributions

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5.1.7: Many-Electron Atoms

Learning Objectives

- Recognize that multi-electron atomics systems present a new complication: electron-electron repulsion!
- Describe how the energy of atomic orbitals in multielectron atoms depend on the values of both *n* and *l*.
- Sketch an orbital energy diagram showing the typical order for a multielectron atom.
- Name the fourth quantum number and it's possible values.
- Clearly state and apply the Pauli Exclusion Principle.

The quantum mechanical model allowed us to determine the energies of the hydrogen atomic orbitals; now we would like to extend this to describe the electronic structure of every element in the Periodic Table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table; however, interactions between electrons make this process a bit more complicated than it sounds. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Orbitals and their Energies

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers *n and l* determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure **5.1.7.1**. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital.



Figure* 5.1.7.1*: *Orbital Energy Level Diagram for a Typical Multielectron Atom*

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shields* an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1*s* orbital, the effective nuclear charge (Z_{eff}) experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 5.1.7.1.

> *Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.*

Notice in Figure 5.1.7.1 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit

(1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. 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**.

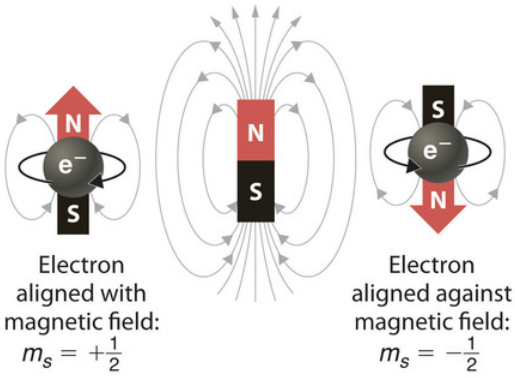


Figure **5.1.7.2**: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure Figure **5.1.7.2**). 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 Pauli Exclusion Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion 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 5.1.7.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an $n = 2p$ 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 $m_l = -l$, $(-l + 1)$,…, $(l - 1)$, 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 5.1.7.1

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

The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell. 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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5.1.8: Electron Configurations

Learning Objectives

- To understand the basics of adding electrons to atomic orbitals
- To understand the basics of the Aufbau principle

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure **5.1.8.1**, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s = −½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

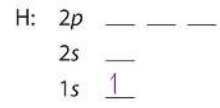
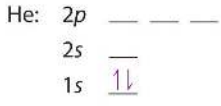


Figure* 5.1.8.1*: *One electron in.*

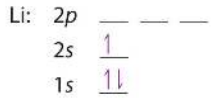
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure **5.1.8.1**), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



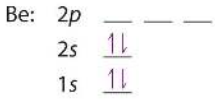
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

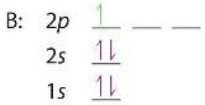


This electron configuration is written as $1s^22s^1$.

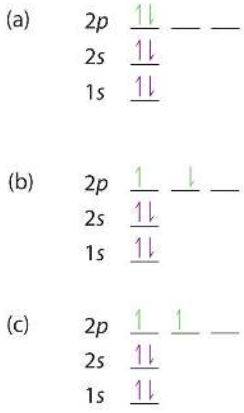
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^22s^2$ electron configuration:



When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:

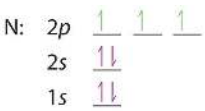


At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?



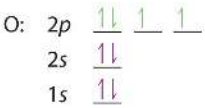
Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

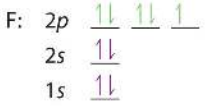


with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

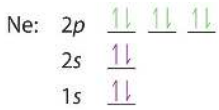
At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Notice that for neon, as for helium, all the orbitals through the $2p$ level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2 2s^2 2p^6 3s^1$, is written as $[Ne]3s^1$:

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6 \mathbf{3}s^1 = [Ne]\mathbf{3}s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the **valence electrons**. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Sodium	$1s^2 2s^2 2p^6 3s^1 = [Ne]3s^1$
Lithium	$1s^2 2s^1 = [He]2s^1$

It is readily apparent that both sodium and lithium have one s electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the $3s$ and $3p$ orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration $[Ne]3s^2 3p^6$, corresponding to a filled valence shell.

Example 5.1.8.1: Electronic Configuration of Phosphorus

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

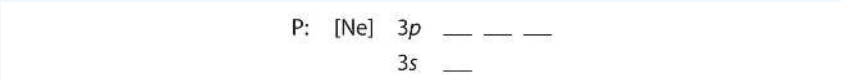
Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
B. Referring to Figure **5.1.8.1**, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

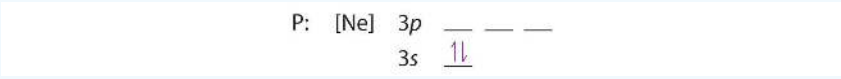
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

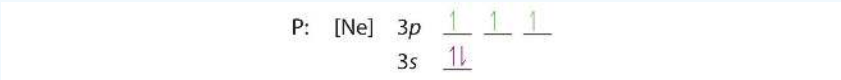
B The additional five electrons are placed in the next available orbitals, which Figure **5.1.8.1** tells us are the 3*s* and 3*p* orbitals:



Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:



The electron configuration is [Ne]$3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

Exercise 5.1.8.1

Draw an orbital diagram and use it to derive the electron configuration of chlorine, Z = 17. What is its valence electron configuration?

Answer

[Ne]$3s^2 3p^5$; $3s^2 3p^5$

The general order in which orbitals are filled is depicted in Figure **5.1.8.2**. Subshells corresponding to each value of n are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton (Z = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

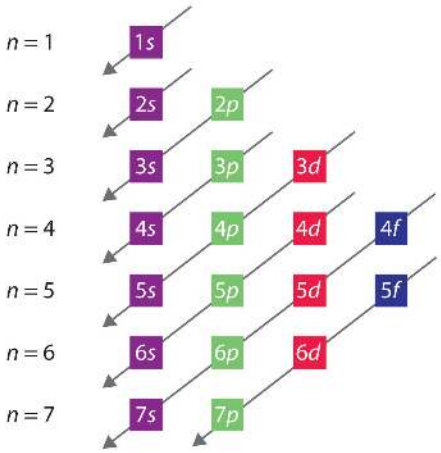


Figure **5.1.8.2**: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next noble gas, radon (Z = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example **5.1.8.2**: Electron Configuration of Mercury

Write the electron configuration of mercury (Z = 80), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure **5.1.8.1** and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure **5.1.8.2** and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure **5.1.8.2**, we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = \text{Hg} = [\text{Xe}]6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise 5.1.8.2: Electron Configuration of Flerovium

Although element 114 is not stable enough to occur in nature, atoms of element 114 were created for the first time in a nuclear reactor in 1998 by a team of Russian and American scientists. The element is named after the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research in Dubna, Russia, where the element was discovered. The name of the laboratory, in turn, honors the Russian physicist Georgy Flyorov. Write the complete electron configuration for element 114.

Answer

$s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure **5.1.8.2**, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure **5.1.8.1**. Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is [Ar]$4s^1 3d^5$ rather than the predicted [Ar]$4s^2 3d^4$. Similarly, the observed electron configuration of copper is [Ar]$4s^1 3d^{10}$ instead of [Ar]$s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. (In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital, as illustrated by Hund's rule.) Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to many additional anomalies. For example, cerium has an electron configuration of [Xe]$6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

> *Additional stability is associated with half-filled or filled subshells.*

Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

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CHAPTER OVERVIEW

5.2: Periodic Properties of the Elements

Last chapter, we presented the contemporary quantum mechanical model of the atom. In using this model to describe the electronic structures of the elements in order of increasing atomic number, we saw that periodic similarities in electron configuration correlate with periodic similarities in properties, which is the basis for the structure of the periodic table. For example, the noble gases have what is often called filled or closed-shell valence electron configurations. These closed shells are actually filled *s* and *p* subshells with a total of eight electrons, which are called *octets*; helium is an exception, with a closed 1*s* shell that has only two electrons. Because of their filled valence shells, the noble gases are generally unreactive. In contrast, the alkali metals have a single valence electron outside a closed shell and readily lose this electron to elements that require electrons to achieve an octet, such as the halogens. Thus because of their periodic similarities in electron configuration, atoms in the same column of the periodic table tend to form compounds with the same oxidation states and stoichiometries. Last chapter ended with the observation that, because all the elements in a column have the same valence electron configuration, the periodic table can be used to find the electron configuration of most of the elements at a glance.

In this chapter, we explore the relationship between the electron configurations of the elements, as reflected in their arrangement in the periodic table, and their physical and chemical properties. In particular, we focus on the similarities between elements in the same column and on the trends in properties that are observed across horizontal rows or down vertical columns. By the end of this chapter, your understanding of these trends and relationships will provide you with clues as to why argon is used in incandescent light bulbs, why coal and wood burst into flames when they come in contact with pure F_2, why aluminum was discovered so late despite being the third most abundant element in Earth's crust, and why lithium is commonly used in batteries. We begin by expanding on the brief discussion of the history of the periodic table and describing how it was created many years before electrons had even been discovered, much less discussed in terms of shells, subshells, orbitals, and electron spin.

5.2.1: Development of the Periodic Table
5.2.2: Shielding and Effective Nuclear Charge
5.2.3: Sizes of Atoms and Ions
5.2.4: Ionization Energy
5.2.5: Electron Affinities
5.2.6: Metals, Nonmetals, and Metalloids
5.2.7: Group Trends for the Active Metals
5.2.8: Group Trends for Selected Nonmetals

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5.2.1: Development of the Periodic Table

Learning Objectives

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

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in 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.

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

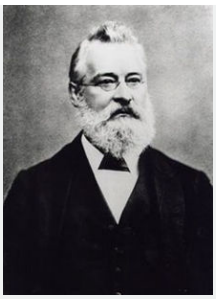
NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

Figure **5.2.1.1**: 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."

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 **5.2.1.1**). Newlands therefore suggested that the elements could be classified into octaves. He described octaves as a group of seven elements which correspond to the horizontal rows in the main groups of today's periodic table. There were seven elements because the noble gases were not known at the time. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

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.



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 **5.2.1.2**), 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):

$$\frac{molar\ mass\ \left(\not{g}/mol\right)}{density\ \left(\not{g}/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{5.2.1.1}$$

As shown in Figure **5.2.1.2**, 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.

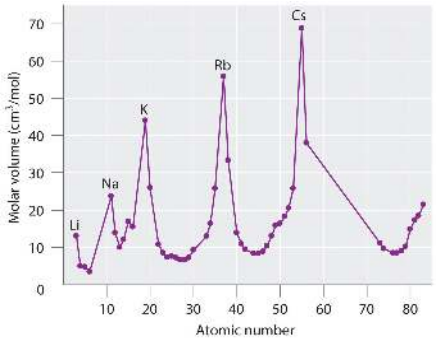
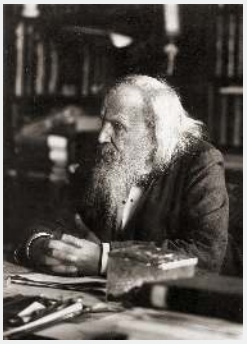


Figure **5.2.1.2**: Variation of Atomic Volume with Atomic Number, Adapted from Meyer’s Plot of 1870**.** Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (Group 1).

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 **5.2.1.3**), 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=40	—	—	—	— — — —
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 **5.2.1.3**: 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 (Figure **5.2.1.1**). 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.

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 **5.2.1.2**: 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.

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 5.2.1.1

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 5.2.1.1

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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5.2.2: Shielding and Effective Nuclear Charge

Learning Objectives

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies. These effects are the underlying basis for the periodic trends in elemental properties that we will explore in this chapter.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Figure **5.2.2.1**). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z. This effect is called electron shielding.

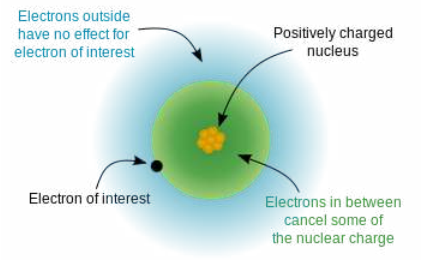


Figure* 5.2.2.1*: *This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; from NikNaks).*

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z-1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z:

$$1 \leq Z_{eff} \leq Z. \tag{5.2.2.1}$$

Notice that $Z_{eff} = Z$ only for hydrogen and only for helium are Z_{eff} and Z comparable in magnitude (Figure **5.2.2.2**).

Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{eff} = Z - S \tag{5.2.2.2}$$

where Z is the atomic number (number of protons in nucleus) and S is the shielding constant. The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from Equation 5.2.2.2 that the effective nuclear charge of an atom increases as the number of protons in an atom increases (Figure 5.2.2.2). Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus. As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

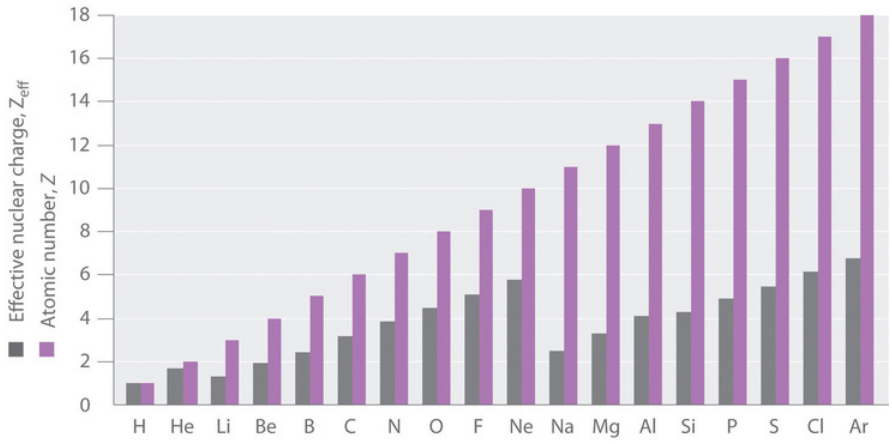


Figure 5.2.2.2: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, (Z_{eff} is always less than Z, and (Z_{eff} increases from left to right as you go across a row.

The shielding constant can be estimated by totaling the screening by **all electrons** (n) except the one in question.

$$S = \sum_{i}^{n-1} S_i \tag{5.2.2.3}$$

where S_i is the shielding of the ith electron.

> *Electrons that are shielded from the full charge of the nucleus experience an effective nuclear charge (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.*

From Equations 5.2.2.2 and 5.2.2.3, Z_{eff} for a specific electron can be estimated is the shielding constants for that electron of all other electrons in species is known. A simple approximation is that all other electrons shield equally and fully:

$$S_i = 1 \tag{5.2.2.4}$$

This crude approximation is demonstrated in Example 5.2.2.1.

Example 5.2.2.1: Fluorine, Neon, and Sodium

What is the effective attraction Z_{eff} experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number A. This is an application of Equations 5.2.2.2 and 5.2.2.3. We use the simple assumption that all electrons shield equally and fully the valence electrons (Equation 5.2.2.4).

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

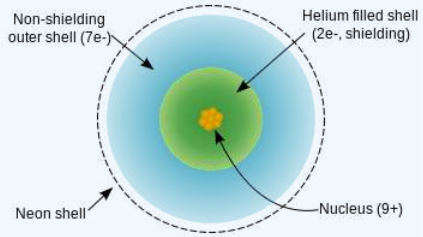


Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA- 3.0; from NikNaks).

- $Z_{\text{eff}}(\text{F}^-) = 9 - 2 = 7+$
- $Z_{\text{eff}}(\text{Ne}) = 10 - 2 = 8+$
- $Z_{\text{eff}}(\text{Na}^+) = 11 - 2 = 9+$

So the sodium cation has the greatest effective nuclear charge. This also suggests that Na^+ has the smallest radius of these species and that is correct.

Exercise 5.2.2.1: Magnesium Species

What is the effective attraction Z_{eff} experienced by the valence electrons in the magnesium anion, the neutral magnesium atom, and magnesium cation? Use the simple approximation for shielding constants in Equations 5.2.2.2 and 5.2.2.3.

Answer

- $Z_{\text{eff}}(\text{Mg}^-) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}^+) = 12 - 10 = 2+$

Remember that the simple approximations in Equations 5.2.2.2 and 5.2.2.3 suggest that valence electrons **do not shield** other valence electrons. Therefore, each of these species has the same number of non-valence electrons and Equations 5.2.2.2 and 5.2.2.3 suggest the effective charge on each valence electron is identical for each of the three species. However, this is not correct!

The fact that these approximations are poor is suggested by the experimental Zeff value shown in Table 5.2.2.1 for Mg. The value is appreciably larger than the +2 estimated above. This indicates that a more complex model is needed to predict the experimental observed Zeff value. The ability of valence electrons to shield (or partially shield) other valence electrons (e.g., Si≠1) shows that the simple approximations used above overestimate the total shielding constant S. A more sophisticated model is needed.

Electron Penetration

The approximation in Equation 5.2.2.4 is a good first order description of electron shielding, but the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 5.2.2.2 for the elements of the first three rows of the periodic table.

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom (Figure 5.2.2.3). Electrons in different orbitals have different electron densities around the nucleus. In other words, penetration depends on the shell (n) and subshell (l).

For example, a 1s electron (Figure 5.2.2.3; purple curve) has greater electron density near the nucleus than a 2p electron (Figure 5.2.2.3; red curve) and has a greater penetration. This related to the shielding constants since the 1s electrons are closer to the nucleus than a 2p electron, hence the 1s screens a 2p electron almost perfectly ($S = 1$. However, the 2s electron has a lower shielding constant ($S < 1$ because it can penetrate close to the nucleus in the small area of electron density within the first spherical node (Figure 5.2.2.3; green curve). In this way the 2s electron can "avoid" some of the shielding effect of the inner 1s electron.

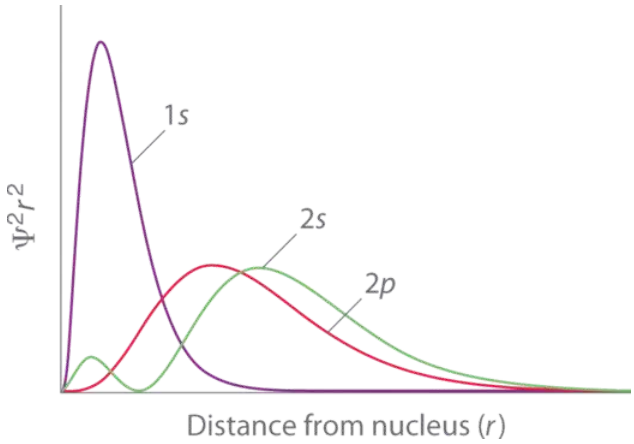


Figure **5.2.2.3**: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital.

For the same shell value (n) the penetrating power of an electron follows this trend in subshells (Figure **5.2.2.3**):

$$s > p > d \approx f. \tag{5.2.2.5}$$

for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f \ \ldots \tag{5.2.2.6}$$

Penetration

Penetration describes the proximity of electrons in an orbital to the nucleus. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.

Table **5.2.2.1**: Effective Nuclear Charges for Selected Atoms

Atom	Sublevel	Z	Z_{eff}
H	1s	1	1
He	1s	2	1.69
Li	1s, 2s	3	2.69, 1.28
Be	1s, 2s	4	3.68, 1.91
B	1s, 2s, 2p	5	4.68, 2.58, 2.42
F	1s, 2s, 2p	9	8.65, 5.13, 5.10
Na	1s, 2s, 2p, 3s	11	10.63, 6.57, 6.80, 2.51

Data from E. Clementi and D. L. Raimondi; The Journal of Chemical Physics 38, 2686 (1963).

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

A Better Estimation of Shielding: Slater Rules

The concepts of electron shielding, orbital penetration and effective nuclear charge were introduced above, but we did so in a qualitative manner (e.g., Equations 5.2.2.5 and 5.2.2.6). A more accurate model for estimating electron shielding and corresponding effective nuclear charge experienced is Slater's Rules. However, the application of these rules is outside the scope of this text.

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

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5.2.3: 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; however, some atoms are larger or smaller than others, and this influences their chemistry. 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 **5.2.3.1** 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.

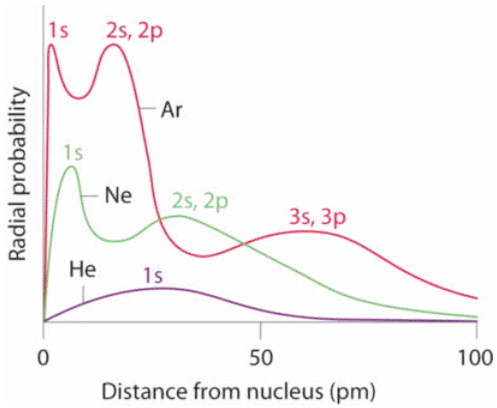


Figure **5.2.3.1**: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another 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 **5.2.3.1** 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 **5.2.3.1** 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 (Figure **5.2.3.2***a*). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1\ Å = 1 \times 10^{-10}\ m = 100\ pm$.

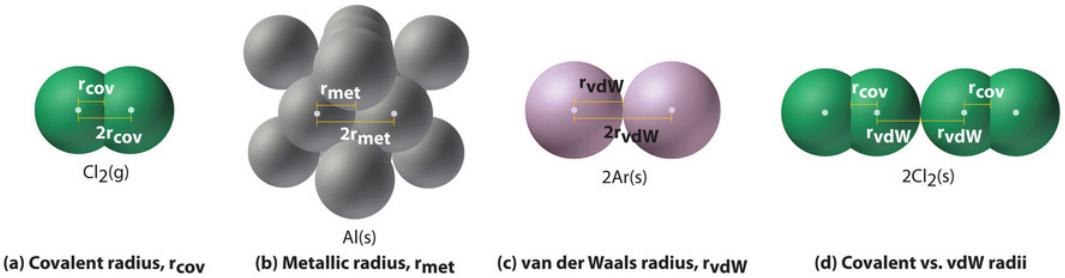


Figure 5.2.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent 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 half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half 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 in the solid (Figure 5.2.3.2*b*). 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 (Figure 5.2.3.2*c*). 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 (Figure 5.2.3.2*d*).

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 5.2.3.3).

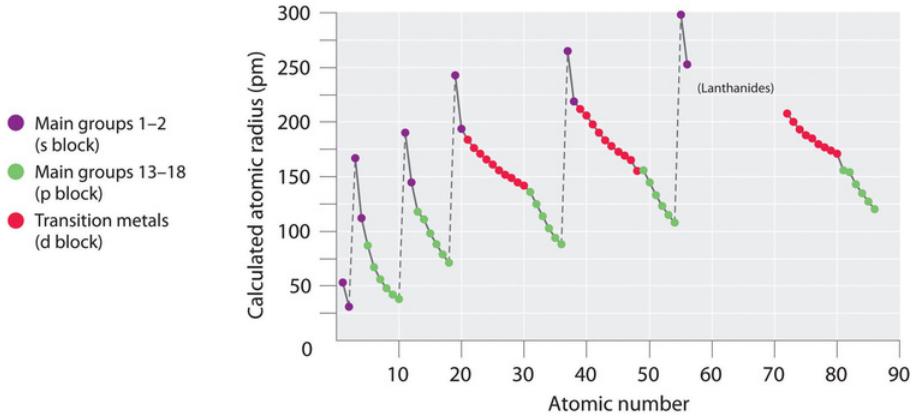


Figure 5.2.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

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 5.2.3.4).

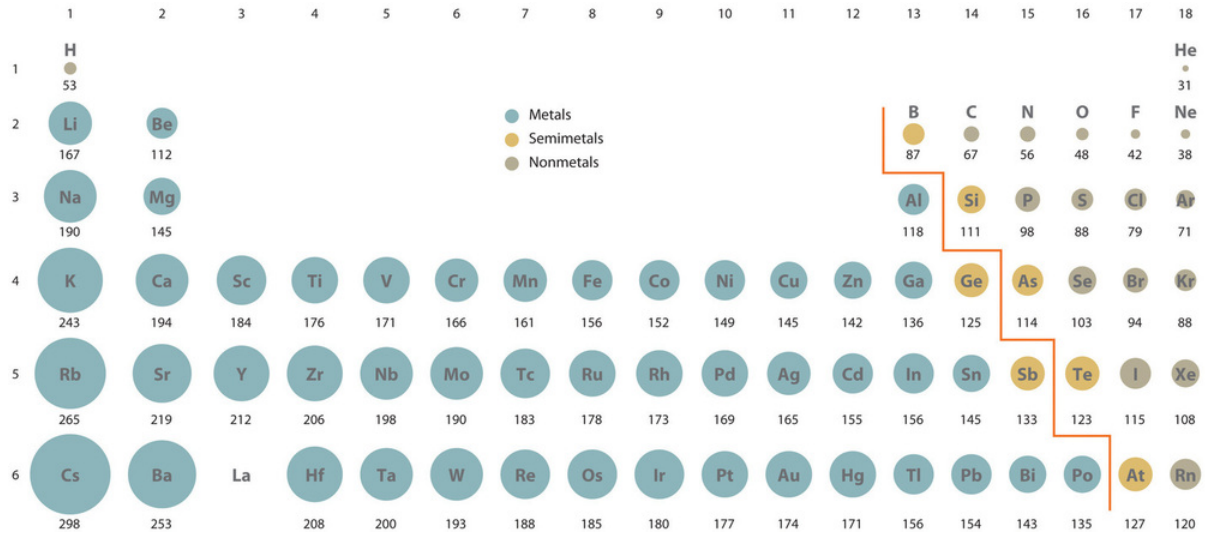


Figure 5.2.3.4 *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent online source for looking up atomic properties.*

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.

> *Atomic radii decrease from left to right across a row and increase from top to bottom down a column.*

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 5.2.3.5).

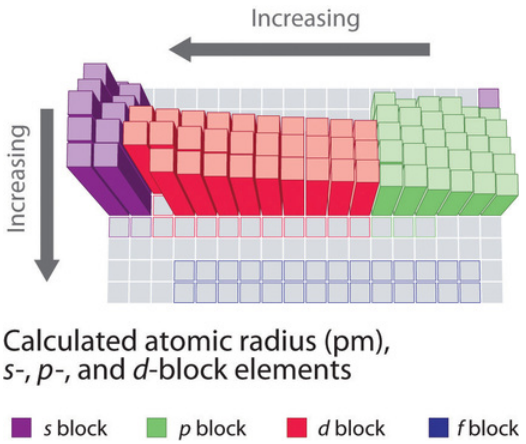


Figure 5.2.3.5: *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

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.

Not all Electrons shield equally

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 5.2.3.1

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 5.2.3.1

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

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). 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.

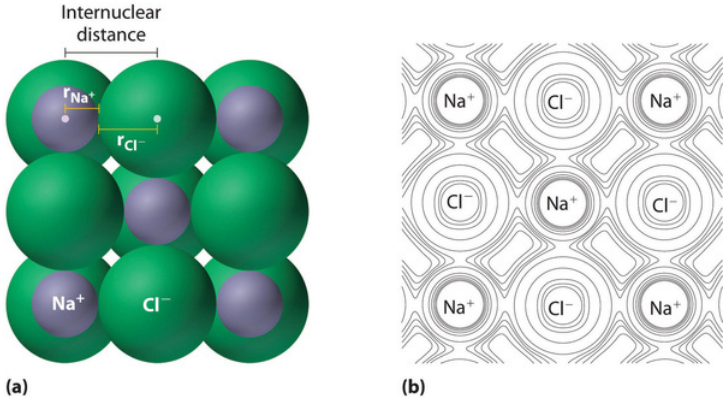


Figure 5.2.3.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours 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^+.

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 5.2.3.6, 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.

A comparison of ionic radii with atomic radii (Figure 5.2.3.7) shows that *a 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 and the ion shrinks (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 and the ion expands (compare F at 42 pm with F^- at 133 pm).

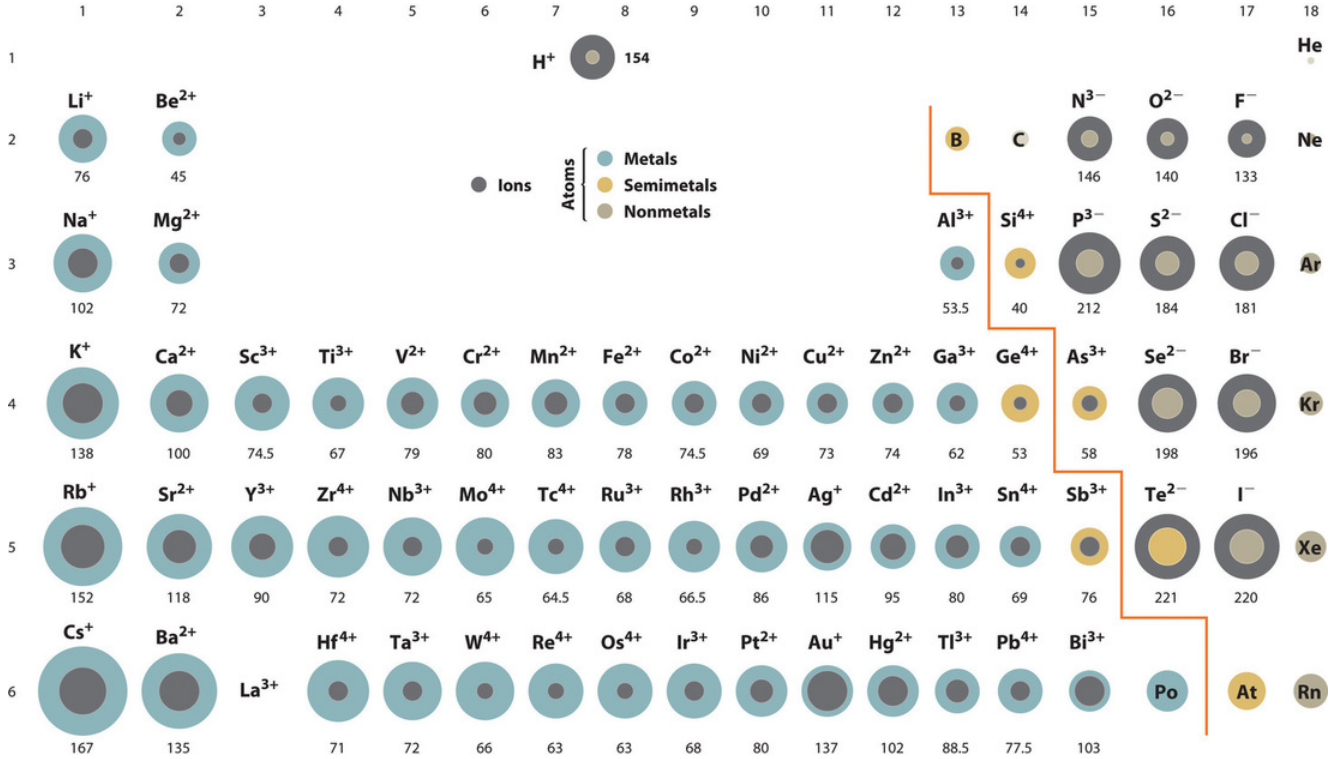


Figure **5.2.3.7**: Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

> *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 **5.2.3.1**. 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.

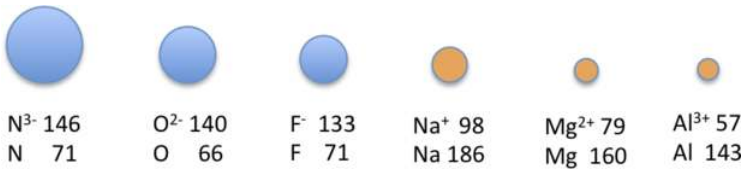
Table **5.2.3.1**: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$
Radius (pm)	102	154*	202†

*The metallic radius measured for Na(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 ($1s^2 2s^2 2p^6$) is shown in Table 5.2.3.3.



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 5.2.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 5.2.3.3: 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 5.2.3.2

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 5.2.3.2

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

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5.2.4: 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. Why is this so? 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

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad \text{energy required=I} \tag{5.2.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 5.2.4.1. 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):

$$1\ eV/atom = 96.49\ kJ/mol \tag{5.2.4.2}$$

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 nth ionization energy (I_n) according to the following reactions:

$$\mathrm{E(g)} \rightarrow \mathrm{E^{+}(g) + e^{-}} \qquad I_1 = \text{1st ionization energy} \tag{5.2.4.3}$$

$$\mathrm{E^{+}(g)} \rightarrow \mathrm{E^{2+}(g) + e^{-}} \qquad I_2 = \text{2nd ionization energy} \tag{5.2.4.4}$$

$$\mathrm{E^{2+}(g)} \rightarrow \mathrm{E^{3+}(g) + e^{-}} \qquad I_3 = \text{3rd ionization energy} \tag{5.2.4.5}$$

Values for the ionization energies of *Li* and *Be* listed in Table 5.2.4.1 show that successive ionization energies for an element increase as they go; 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.

> *Successive ionization energies for an element* ***increase****.*

Table 5.2.4.1: 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	Reaction	Electronic Transition	I
$\mathrm{Li\ (g) \rightarrow Li^{+}(g) + e^{-}}$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be(g) \rightarrow Be^{+}(g) + e^{-}}$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$\mathrm{Li^{+}(g) \rightarrow Li^{2+}(g) + e^{-}}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^{+}(g) \rightarrow Be^{2+}(g) + e^{-}}$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}(g) \rightarrow Li^{3+}(g) + e^{-}}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^{-}}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}(g) \rightarrow Be^{4+}(g) + e^{-}}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table 5.2.4.1 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**:

$$Li^+(g) \rightarrow Li^{2+}(g) + e^- \tag{5.2.4.6}$$

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**:

$$Be^{2+}(g) \rightarrow Be^{3+}(g) + e^- \tag{5.2.4.7}$$

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.*

> *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 **5.2.4.2**): 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 **5.2.4.2**. 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 **5.2.4.2**: 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	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
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 **5.2.4.1**: 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:

$$E_{(g)}^{3+} \rightarrow E_{(g)}^{4+} + e^- \tag{5.2.4.8}$$

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 5.2.4.1: 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 **5.2.4.2** 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.

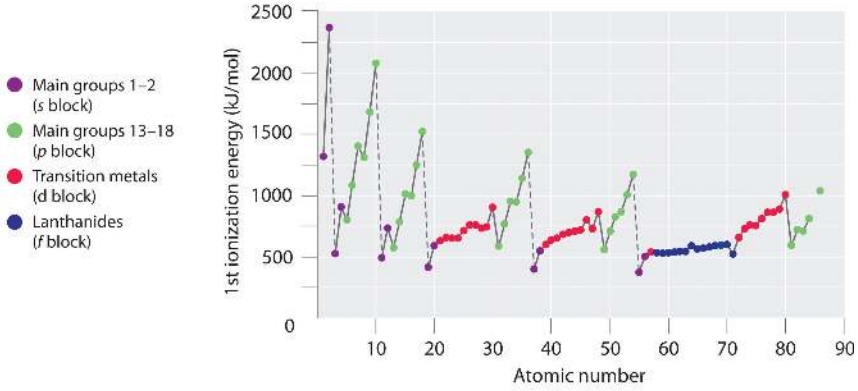


Figure **5.2.4.1**: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electron configurations of these "exceptions" provide the answer why. 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

and the *p* electron is more easily removed. 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.

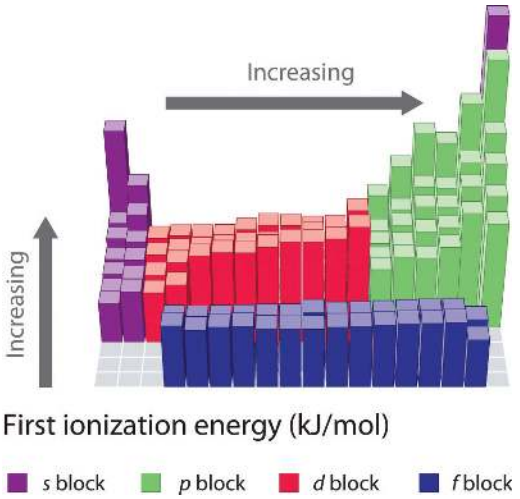
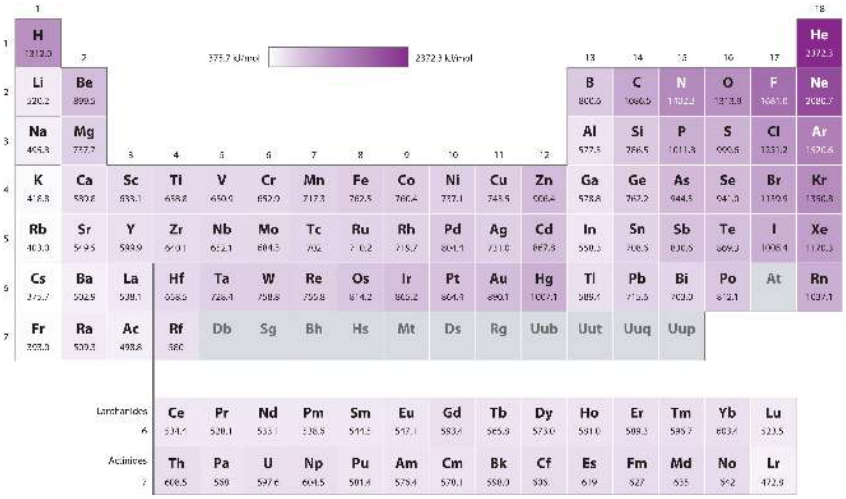


***Figure* 5.2.4.2:** *First Ionization Energies of the s-, p-, d-, and f-Block Elements*

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 7.4.1 and are presented numerically and graphically in Figure **5.2.4.2**. 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).
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 typically 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).



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).

> *Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.*

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, shielding 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 5.2.4.2: 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 5.2.4.2: 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

Summary

The tendency of an element to lose electrons 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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5.2.5: Electron Affinities

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to add 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 or ion:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA \tag{5.2.5.1}$$

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 (Figure 5.2.5.1).

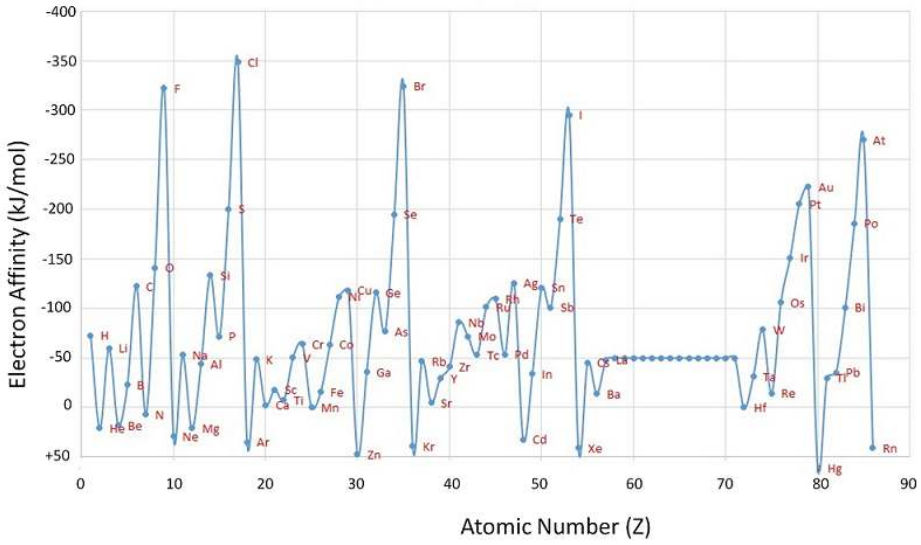


Figure 5.2.5.1***:*** *A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).*

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:

$$\mathrm{Cl(g) + e^- \rightarrow Cl^-(g)} \qquad EA = -346\ kJ/mol \tag{5.2.5.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be(g) + e^- \rightarrow Be^-(g)} \qquad EA \geq 0 \tag{5.2.5.3}$$

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:

$$\mathrm{N(g) + e^- \rightarrow N^-(g)} \qquad EA \approx 0 \tag{5.2.5.4}$$

> *Generally, electron affinities become more negative across a row of the periodic table.*

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.

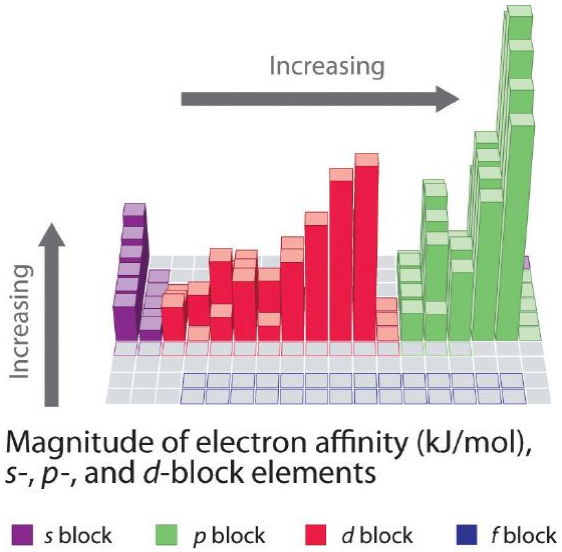


***Figure* 5.2.5.2:** *Electron Affinities (in kJ/mol) of the s-, p-, and d-Block Elements.*

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.

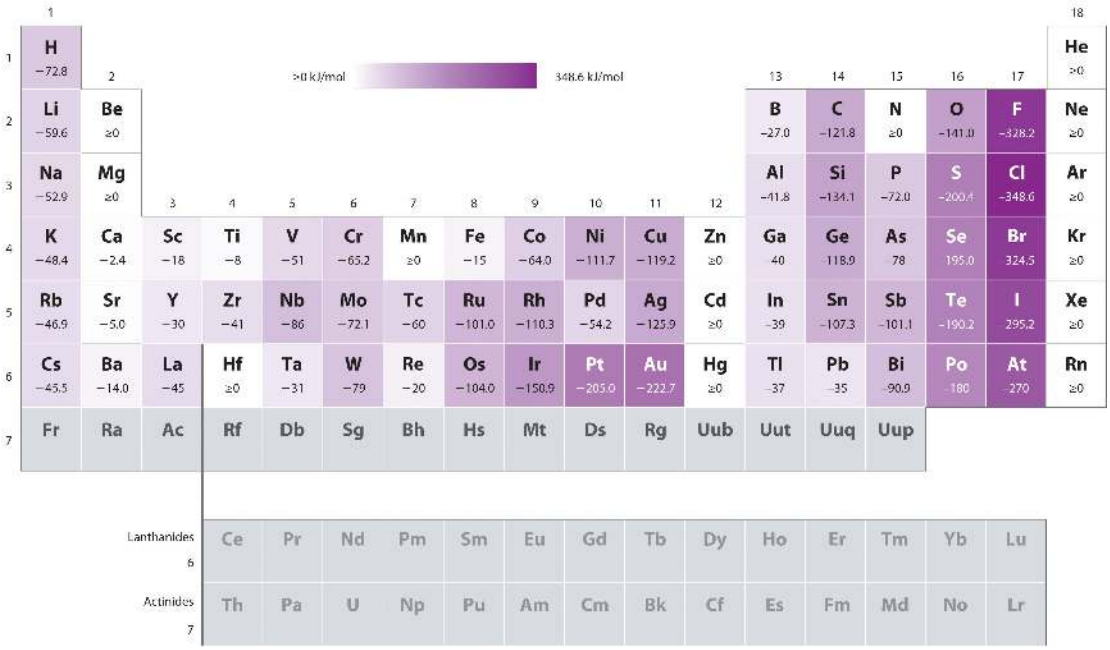


Figure 5.2.5.3: *There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).*

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{5.2.5.5}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{5.2.5.6}$$

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:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{5.2.5.7}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{5.2.5.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{5.2.5.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

> *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 cations 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 5.2.5.1: 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 5.2.5.1: 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

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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5.2.6: Metals, Nonmetals, and Metalloids

Learning Objectives

- To understand the basic properties separating Metals from Nonmetals and Metalloids

An element is the simplest form of matter that cannot be split into simpler substances or built from simpler substances by any ordinary chemical or physical method. There are 118 elements known to us, out of which 92 are naturally occurring, while the rest have been prepared artificially. Elements are further classified into metals, non-metals, and metalloids based on their properties, which are correlated with their placement in the periodic table.

Table **5.2.6.1**: Characteristic properties of metallic and non-metallic elements:

Metallic Elements	Nonmetallic elements
Distinguishing luster (shine)	Non-lustrous, various colors
Malleable and ductile (flexible) as solids	Brittle, hard or soft
Conduct heat and electricity	Poor conductors
Metallic oxides are basic, ionic	Nonmetallic oxides are acidic, covalent
Form cations in aqueous solution	Form anions, oxyanions in aqueous solution

Metals

With the exception of hydrogen, all elements that form positive ions by losing electrons during chemical reactions are called metals. Thus metals are electropositive elements with relatively low ionization energies. They are characterized by bright luster, hardness, ability to resonate sound and are excellent conductors of heat and electricity. Metals are solids under normal conditions except for Mercury.

Physical Properties of Metals

Metals are lustrous, malleable, ductile, good conductors of heat and electricity. Other properties include:

- **State**: Metals are solids at room temperature with the exception of mercury, which is liquid at room temperature (Gallium is liquid on hot days).
- **Luster**: Metals have the quality of reflecting light from their surface and can be polished e.g., gold, silver and copper.
- **Malleability:** Metals have the ability to withstand hammering and can be made into thin sheets known as foils. For example, a sugar cube sized chunk of gold can be pounded into a thin sheet that will cover a football field.
- **Ductility:** Metals can be drawn into wires. For example, 100 g of silver can be drawn into a thin wire about 200 meters long.
- **Hardness:** All metals are hard except sodium and potassium, which are soft and can be cut with a knife.
- **Valency:** Metals typically have 1 to 3 electrons in the outermost shell of their atoms.
- **Conduction**: Metals are good conductors because they have free electrons. Silver and copper are the two best conductors of heat and electricity. Lead is the poorest conductor of heat. Bismuth, mercury and iron are also poor conductors
- **Density**: Metals have high density and are very heavy. Iridium and osmium have the highest densities whereas lithium has the lowest density.
- **Melting and Boiling Points**: Metals have high melting and boiling points. Tungsten has the highest melting and boiling points whereas mercury has the lowest. Sodium and potassium also have low melting points.

Chemical Properties of Metals

Metals are electropositive elements that generally form *basic* or *amphoteric* oxides with oxygen. Other chemical properties include:

- **Electropositive Character**: Metals tend to have low ionization energies, and *typically lose electrons (i.e. are **oxidized**) when they undergo chemical reactions* They normally do not accept electrons. For example:
  - Alkali metals are always 1^+ (lose the electron in *s* subshell)

- Alkaline earth metals are always 2^+ (lose both electrons in *s* subshell)
- Transition metal ions do not follow an obvious pattern, 2^+ is common (lose both electrons in *s* subshell), and 1^+ and 3^+ are also observed

$$\mathrm{Na^0 \rightarrow Na^+ + e^-}$$

$$\mathrm{Mg^0 \rightarrow Mg^{2+} + 2\,e^-}$$

$$\mathrm{Al^0 \rightarrow Al^{3+} + 3\,e^-}$$

Compounds of metals with non-metals tend to be ***ionic*** in nature. Most metal oxides are basic oxides and dissolve in water to form ***metal hydroxides***:

$$\mathrm{Na_2O\,(s) + H_2O\,(l) \rightarrow 2\,NaOH\,(aq)}$$

$$\mathrm{CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(aq)}$$

Metal oxides exhibit their ***basic*** chemical nature by reacting with ***acids*** to form metal ***salts*** and water:

$$\mathrm{MgO\,(s) + HCl\,(aq) \rightarrow MgCl_2\,(aq) + H_2O\,(l)}$$

$$\mathrm{NiO\,(s) + H_2SO_4\,(aq) \rightarrow NiSO_4\,(aq) + H_2O\,(l)}$$

Example 5.2.6.1

What is the chemical formula for aluminum oxide?

Solution

Al has a 3+ charge, the oxide ion is O^{2-}, thus Al_2O_3.

Example 5.2.6.2

Would you expect it to be solid, liquid or gas at room temperature?

Solutions

Oxides of metals are characteristically solid at room temperature

Example 5.2.6.3

Write the balanced chemical equation for the reaction of aluminum oxide with nitric acid:

Solution

Metal oxide + acid -> salt + water

$$\mathrm{Al_2O_3\,(s) + 6\,HNO_3\,(aq) \rightarrow 2\,Al(NO_3)_3\,(aq) + 3\,H_2O\,(l)}$$

Nonmetals

Elements that tend to gain electrons to form anions during chemical reactions are called non-metals. These are electronegative elements with high ionization energies. They are non-lustrous, brittle and poor conductors of heat and electricity (except graphite). Non-metals can be gases, liquids or solids.

Physical Properties of Nonmetals

- **Physical State**: Most of the non-metals exist in two of the three states of matter at room temperature: gases (oxygen) and solids (carbon). Only bromine exists as a liquid at room temperature.
- **Non-Malleable and Ductile**: Non-metals are very brittle, and cannot be rolled into wires or pounded into sheets.
- **Conduction**: They are poor conductors of heat and electricity.
- **Luster:** These have no metallic luster and do not reflect light.
- **Melting and Boiling Points**: The melting points of non-metals are *generally* lower than metals, but are highly variable.

- Seven non-metals exist under standard conditions as *diatomic molecules*: $\mathbf{H_2\,(g)}$, $\mathbf{N_2\,(g)}$, $\mathbf{O_2\,(g)}$, $\mathbf{F_2\,(g)}$, $\mathbf{Cl_2\,(g)}$, $\mathbf{Br_2\,(l)}$, $\mathbf{I_2\,(s)}$.

Chemical Properties of Nonmetals

Non-metals have a tendency to gain or share electrons with other atoms. They are electronegative in character. Nonmetals, when reacting with metals, tend to gain electrons (typically *attaining noble gas electron configuration)* and become ***anions:***

$$\mathbf{3\,Br_2\,(l) + 2\,Al\,(s) \rightarrow 2\,AlBr_3\,(s)}$$

Compounds composed entirely of nonmetals are covalent substances. They generally form acidic or neutral oxides with oxygen that that dissolve in water to form acids:

$$\mathbf{CO_2\,(g) + H_2O\,(l) \rightarrow \underset{\text{carbonic acid}}{H_2CO_3\,(aq)}}$$

As you may know, carbonated water is slightly acidic (carbonic acid).

Nonmetal oxides can combine with bases to form salts.

$$\mathbf{CO_2\,(g) + 2\,NaOH\,(aq) \rightarrow Na_2CO_3\,(aq) + H_2O\,(l)}$$

Metalloids

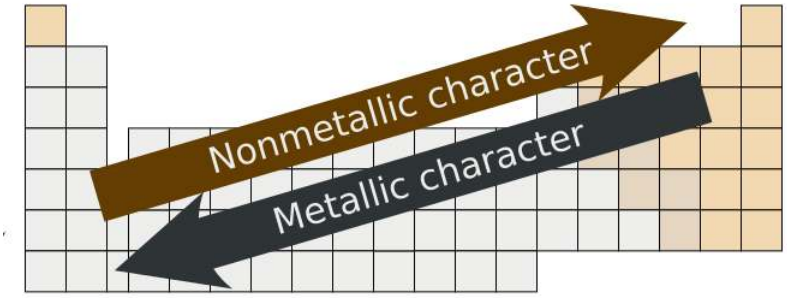
Metalloids have properties intermediate between the metals and nonmetals. Metalloids are useful in the semiconductor industry. Metalloids are all solid at room temperature. They can form alloys with other metals. Some metalloids, such as silicon and germanium, can act as electrical conductors under the right conditions, thus they are called semiconductors. Silicon for example appears lustrous, but is *not* malleable nor ductile (it is *brittle* - a characteristic of some nonmetals). It is a much poorer conductor of heat and electricity than the metals. The physical properties of metalloids tend to be metallic, but their chemical properties tend to be non-metallic. The oxidation number of an element in this group can range from +5 to -2, depending on the group in which it is located.

Table **5.2.6.2**: Elements categorized into metals, non-metals and metalloids.

Metals	Non-metals	Metalloids
Gold	Oxygen	Silicon
Silver	Carbon	Boron
Copper	Hydrogen	Arsenic
Iron	Nitrogen	Antimony
Mercury	Sulfur	Germanium
Zinc	Phosphorus	

Trends in Metallic and Nonmetallic Character

Metallic character is strongest for the elements in the leftmost part of the periodic table, and tends to decrease as we move to the right in any period (nonmetallic character increases with increasing electronegativity and ionization energy values). Within any group of elements (columns), the metallic character increases from top to bottom (the electronegativity and ionization energy values generally decrease as we move down a group). This general trend is not necessarily observed with the transition metals.



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5.2.7: Group Trends for the Active Metals

The elements within the same group of the periodic table tend to exhibit similar physical and chemical properties. Four major factors affect reactivity of metals: nuclear charge, atomic radius, shielding effect and sublevel arrangement (of electrons). Metal reactivity relates to ability to lose electrons (oxidize), form basic hydroxides, form ionic compounds with non-metals. In general, the bigger the atom, the greater the ability to lose electrons. The greater the shielding, the greater the ability to lose electrons. Therefore, metallic character increases going down the table, and decreases going across -- so the most active metal is towards the left and down.

Group 1: The Alkali Metals

The word "alkali" is derived from an Arabic word meaning "ashes". Many sodium and potassium compounds were isolated from wood ashes (Na_2CO_3 and K_2CO_3 are still occasionally referred to as "soda ash" and "potash"). In the alkali group, as we go down the group we have elements Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr). Several physical properties of these elements are compared in Table **5.2.7.1**. These elements have all only one electron in their outermost shells. All the elements show metallic properties and have valence +1, hence they give up electron easily.

Table **5.2.7.1**: General Properties of Group I Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius	Ionization Energy (kJ/mol)
Lithium	$[He]2s^1$	181	0.53	1.52	520
Sodium	$[Ne]3s^1$	98	0.97	1.86	496
Potassium	$[Ar]4s^1$	63	0.86	2.27	419
Rubidium	$[Kr]5s^1$	39	1.53	2.47	403
Cesium	$[Xe]6s^1$	28	1.88	2.65	376

As we move down the group (from Li to Fr), the following trends are observed (Table **5.2.7.1**):

- All have a single electron in an 's' valence orbital
- The melting point decreases
- The density increases
- The atomic radius increases
- The ionization energy decreases (first ionization energy)

> *The alkali metals have the lowest I_1 values of the elements*

This represents the relative ease with which the lone electron in the outer 's' orbital can be removed.

The alkali metals are very reactive, readily losing 1 electron to form an ion with a 1+ charge:

$$M \rightarrow M^+ + e- \tag{5.2.7.1}$$

Due to this reactivity, the alkali metals are found in nature only as compounds. The alkali metals combine directly with most nonmetals:

- React with hydrogen to form solid *hydrides*

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH(s) \tag{5.2.7.2}$$

(Note: hydrogen is present in the metal hydride as the ***hydride*** H^- ion)

- React with sulfur to form solid *sulfides*

$$2M_{(s)} + S_{(s)} \rightarrow M_2S_{(s)} \tag{5.2.7.3}$$

React with chlorine to form solid *chlorides*

$$2M_{(s)} + Cl_{2(g)} \rightarrow 2MCl_{(s)} \tag{5.2.7.4}$$

Alkali metals react with water to produce hydrogen gas and alkali metal hydroxides; this is a very exothermic reaction (Figure 5.2.7.1).

$$2M_{(s)} + 2H_2O_{(l)} \rightarrow 2MOH_{(aq)} + H_{2(g)} \tag{5.2.7.5}$$

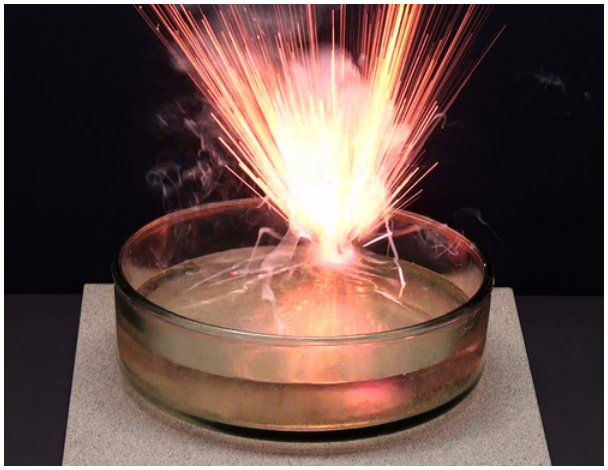


Figure 5.2.7.1: A small piece of potassium metal explodes as it reacts with water. (CC SA-BY 3.0; Tavoromann)

The reaction between alkali metals and oxygen is more complex:

- A common reaction is to form metal oxides which contain the O^{2-} ***ion***

$$4Li_{(s)} + O_{2(g)} \rightarrow \underbrace{2Li_2O_{(s)}}_{\text{lithium oxide}} \tag{5.2.7.6}$$

Other alkali metals ***can*** form metal peroxides (contains O_2^{2-} ion)

$$2Na(s) + O_{2(g)} \rightarrow \underbrace{Na_2O_{2(s)}}_{\text{sodium peroxide}} \tag{5.2.7.7}$$

K, Rb and Cs ***can*** also form superoxides (O_2^- ion)

$$K(s) + O_{2(g)} \rightarrow \underbrace{KO_{2(s)}}_{\text{potassium superoxide}} \tag{5.2.7.8}$$

Colors via Absorption

The color of a chemical is produced when a valence electron in an atom is excited from one energy level to another by visible radiation. In this case, the particular frequency of light that excites the electron is ***absorbed***. Thus, the remaining light that you see is white light devoid of one or more wavelengths (thus appearing colored). Alkali metals, having lost their outermost electrons, have no electrons that can be excited by visible radiation. Alkali metal salts and their aqueous solution are colorless unless they contain a colored anion.

Colors via Emission

When alkali metals are placed in a flame the ions are reduced (gain an electron) in the lower part of the flame. The electron is excited (jumps to a higher orbital) by the high temperature of the flame. When the excited electron falls back down to a lower orbital a photon is released. The transition of the valence electron of sodium from the 3p down to the 3s subshell results in release of a photon with a wavelength of 589 nm (yellow)

Flame colors:

- Lithium: crimson red

- Sodium: yellow
- Potassium: lilac

Group 2: The Alkaline Earth Metals

Compared with the alkali metals, the alkaline earth metals are typically harder, more dense, melt at a higher temperature. The first ionization energies (I_1) of the alkaline earth metals are not as low as the alkali metals. The alkaline earth metals are therefore less reactive than the alkali metals (Be and Mg are the least reactive of the alkaline earth metals). Several physical properties of these elements are compared in Table **5.2.7.2**.

Table **5.2.7.2**: General Properties of Group 2 Metals

Element	Electronic Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius	Ionization Energy (kJ/mol)
Beryllium	$[He]2s^2$	1278	1.85	1.52	899
Magnesium	$[Ne]3s^2$	649	1.74	1.60	738
Calcium	$[Ar]4s^2$	839	1.54	1.97	590
Strontium	$[Kr]5s^2$	769	2.54	2.15	549
Barium	$[Xe]6s^2$	725	3.51	2.17	503

Calcium, and elements below it, react readily with water at room temperature:

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)} \tag{5.2.7.9}$$

The tendency of the alkaline earths to lose their two valence electrons is demonstrated in the reactivity of Mg towards chlorine gas and oxygen:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} \tag{5.2.7.10}$$

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)} \tag{5.2.7.11}$$

The 2+ ions of the alkaline earth metals have a noble gas like electron configuration and are thus form colorless or white compounds (unless the anion is itself colored). Flame colors:

- Calcium: brick red
- Strontium: crimson red
- Barium: green

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5.2.8: Group Trends for Selected Nonmetals

Learning Objectives

- To gain a descriptive understanding of the chemical properties of Hydrogen, the group 16, 17 and 18 elements.

Non-metallic character is the ability to be reduced (be an oxidizing agent), form acidic hydroxides, form covalent compounds with non-metals. These characteristics increase with a larger nuclear charge and smaller radius, with no increase in shielding. The most active non-metal would be the one farthest up and to the right -- not including the noble gases (non-reactive.)

Hydrogen

Hydrogen has a $1s^1$ electron configuration and is placed above the alkali metal group. Hydrogen is a ***non-metal***, which occurs as a ***gas*** (H_2) under normal conditions.

- Its ionization energy is considerably higher (due to lack of shielding, and thus higher Z_{eff}) than the rest of the Group 1 metals and is more like the ***nonmetals***
- Hydrogen generally reacts with other nonmetals to form molecular compounds (typically highly exothermic)
- Hydrogen reacts with active metals to form metal hydrides which contain the H^- ***hydride ion***:

$$2Na_{(s)} + H_{2(g)} \rightarrow 2NaH_{(s)} \tag{5.2.8.1}$$

- Hydrogen can also lose an electron to yield the aqueous $H^+_{(aq)}$ hydronium ion.

Group 16: The Oxygen Family

As we proceed down group 16 the elements become more metallic in nature:

- Oxygen is a gas, the rest are solids
- Oxygen, sulfur and selenium are nonmetals
- Tellurium is a metalloid with some metal properties
- Polonium is a metal

Oxygen can be found in two molecular forms, O_2 and O_3 (ozone). These two forms of oxygen are called ***allotropes*** (*different forms of the same element in the same state*)

$$3O_{2(g)} \rightarrow 2O_{3(g)} \quad \Delta H = 284.6\ kJ/mol \tag{5.2.8.2}$$

the reaction is endothermic, thus ozone is less stable that O_2

> Oxygen has a great tendency to attract electrons from other elements (i.e. to "oxidize" them)

- Oxygen in combination with metals is almost always present as the O^{2-} ion (which has noble gas electronic configuration and is particularly stable)
- Two other oxygen anions are observed: ***peroxide (O_2^{2-}) and superoxide (O_2^-)***

Sulfur

Sulfur also exists in several allotropic forms, the most common stable allotrope is the yellow solid S_8 (an 8 member ring of sulfur atoms). Like oxygen, ***sulfur has a tendency to gain electrons*** from other elements, and to form ***sulfides*** (which contain the S^{2-} ion). This is particular true for the active metals:

$$16Na_{(s)} + S_{8(s)} \rightarrow 8Na_2S_{(s)} \tag{5.2.8.3}$$

Note: most sulfur in nature is present as a metal-sulfur compound. Sulfur chemistry is more complex than that of oxygen.

Group 17: The Halogens

"Halogen" is derived from the Greek meaning "salt formers"

- Astatine is radioactive and rare, and some of its properties are unknown

- All the halogens are ***nonmetals***
- Each element consists of diatomic molecules under standard conditions

Colors of diatomic halogens: (*not* flame colors)

- Fluorine: pale yellow
- Chlorine: yellow green
- Bromine: reddish brown
- Iodine: violet vapor

The halogens have some of the most negative electron affinities (i.e. large exothermic process in gaining an electron from another element)

$$X_2 + 2e^- \rightarrow 2X^- \tag{5.2.8.4}$$

- Fluorine and chlorine are the most reactive halogens (highest electron affinities). Fluorine will remove electrons from almost any substance (including several of the noble gases from Group 18).

Note

The chemistry of the halogens is dominated by their tendency to gain electrons from other elements (forming a halide ion)

In 1992, **22.3 billion pounds** of chlorine was produced. Both chlorine and sodium can be produced by electrolysis of molten sodium chloride (table salt). The electricity is used to strip electrons from chloride ions and transfer them to sodium ions to produce chlorine gas and solid sodium metal

Chlorine reacts slowly with water to produce hydrochloric acid and hypochlorous acid:

$$Cl_{2(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HOCl_{(aq)}.5 \tag{5.2.8.5}$$

Hypochlorous acid is a disinfectant, thus chlorine is a useful addition to swimming pool water

The halogens react with most metals to form ionic halides:

$$Cl_{2(g)} + 2Na_{(s)} \rightarrow 2NaCl_{(s)} \tag{5.2.8.6}$$

Group 18: The Noble Gases

- Nonmetals
- Gases at room temperature
- monoatomic
- completely filled 's' and 'p' subshells
- large first ionization energy, ***but this decreases somewhat as we move down the group***

Rn is highly radioactive and some of its properties are unknown

They are exceptionally unreactive. It was reasoned that if any of these were reactive, they would most likely be Rn, Xe or Kr where the first ionization energies were lower.

Note

In order to react, they would have to be combined with an element which had a high tendency to remove electrons from other atoms. Such as fluorine.

Compounds of noble gases to date:

$$XeF_2\ XeF_4\ XeF_6$$

only one compound with Kr has been made

$$KrF_2$$

No compounds observed with He, Ne, or Ar; they are truly inert gases.

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SECTION OVERVIEW

Topic F- Molecular Structure

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

General Covalent Bonding Concepts

1. Understand the relationship between potential energy and internuclear distance.
2. Understand a covalent bond in terms of potential energy.
3. Recognize that there are two models used to describe covalent bonding: (1) valence bond theory and (2) molecular orbital theory.

Localized Electron Model of Covalent Bonding

4. Draw reasonable Lewis structures for small molecules and common polyatomic ions.
5. Determine bond order.
6. Determine bond polarity.
7. Apply the concept of bond energies to estimate ΔH for any reaction.
8. Understand the relationship between bond order, bond distance, and bond energy.
9. Use VSEPR Theory to predict the 3D molecular geometry.
10. Determine if a molecule is polar.
11. Use resonance structures to show electron delocalization. Use formal charges to determine major and minor resonance contributors.
12. Use **atomic orbital overlap** to model a covalent bond. (Valence Bond Theory)
13. Use orbital hybridization to rationalize orbital geometry with the observed bond angles.
14. Identify and describe a sigma bond and a pi bond in terms of orbital overlap.
15. Overall, predict the following for a given Lewis structure:
    - The molecular geometry for a central bonding atom, including typical bond angles.
    - Whether the molecular geometry is likely to be distorted.
    - The orbital geometry and corresponding orbital hybridization (sp, sp^2, sp^3, etc.) that will align with the bond geometry for a central bonding atom.
    - Whether or not the molecule is polar.

Delocalized Electron Model of Covalent Bonding

15. Use **molecular orbitals** to model a covalent bond. (Molecule Orbital Theory)
16. Use MO energy diagrams to determine bond order and magnetic properties of a molecule.
17. Draw sketches of the molecular orbitals for diatomic molecules that are formed from linear combinations of two atomic orbitals, and identify each as bonding or antibonding.

6.1: Basic Concepts of Covalent Bonding

6.1.1: Covalent Bonding Fundamentals
6.1.2: Interpreting Lewis Structures
6.1.3: Drawing Lewis Structures
6.1.4: Resonance Lewis Structures
6.1.5: Strength of Covalent Bonds
6.1.6: The VSEPR Model
6.1.7: Molecular Polarity

6.1.8: A Different Perspective on Drawing Lewis Structures

6.2: Orbitals and Bonding Theories

6.2.1: Localized Electron Model of Covalent Bonding
6.2.2: Hybrid Atomic Orbitals
6.2.3: Orbital Overlap in Multiple Bonds
6.2.4: Molecular Orbital Theory

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CHAPTER OVERVIEW

6.1: Basic Concepts of Covalent Bonding

6.1.1: Covalent Bonding Fundamentals
6.1.2: Interpreting Lewis Structures
6.1.3: Drawing Lewis Structures
6.1.4: Resonance Lewis Structures
6.1.5: Strength of Covalent Bonds
6.1.6: The VSEPR Model
6.1.7: Molecular Polarity
6.1.8: A Different Perspective on Drawing Lewis Structures

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6.1.1: Covalent Bonding Fundamentals

Learning Objectives

- Understand the relationship between potential energy and internuclear distance.
- Understand a covalent bond in terms of potential energy.
- Recognize that there are two models used to describe covalent bonding: valence bond theory and molecular orbital theory

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.

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.

In this chapter, we will focus on covalent bonding.

Covalent Bonding

A covalent bond is the sharing of electrons between two atoms. The electrons are the "glue" that keeps the two atoms together. When two atoms share electrons, the shared electrons create a region of higher electron density between the nuclei of the atoms. This concentration of negative charge pulls the nuclei together. The nuclei do not get too close to each other, however, because they repel each other. At some distance, the attraction and the repulsion balance each other, forming a stable bond.

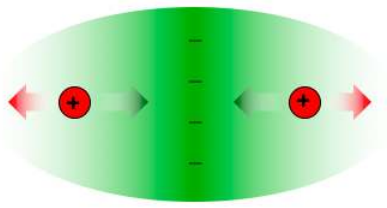


Figure **6.1.1.1**: The two nuclei (red) are attracted to the high electron density in the center of the molecule (green arrows), but repelled by each other (red arrows).

Bond Energies

Fundamentally, atoms form a chemical bond because the overall energy of the bonded atoms is lower than the overall energy of the original, unbonded atoms. For example, an H_2 molecule has a lower energy than two H atoms. We can show how the potential energy of two atoms depends on the distance between them by drawing a bond energy diagram. The bond energy diagram for H_2 is shown below:

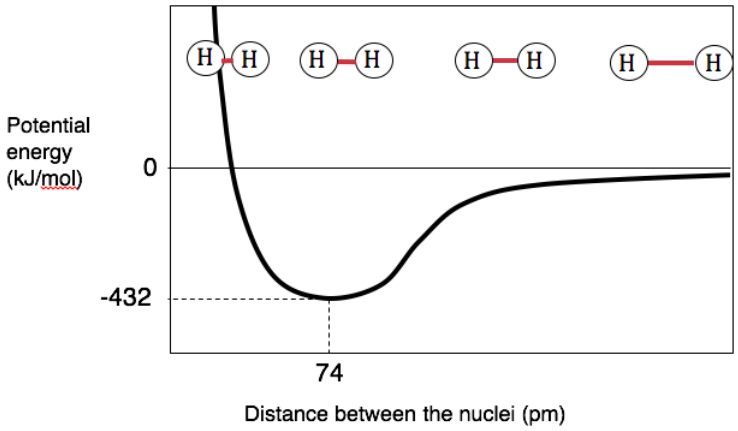


Figure **6.1.1.2**: Bond energy diagram for two hydrogen atoms as a function of internuclear distance.

When charged particles interact, electrostatic forces determine the potential energy of the system. According to **Coulomb's Law**, the energy of the electrostatic attraction (***E***) between two charged particles is proportional to the magnitude of the charges and inversely proportional to the internuclear distance between the particles (***r***):

$$E \propto \frac{Q_1 Q_2}{r} \tag{6.1.1.1}$$

where each particle's charge is represented by the symbol Q. If Q_1 and Q_2 have opposite signs (as an electron and a proton, where Q_1 is −1 for an elecctron and Q_2 is +1 for a proton), then E is negative, which means that energy is *released* when oppositely charged particles are brought together from an infinite distance to form an isolated pair. The opposite is true for like-charged particles. Figure **6.1.1.2** considers all of the the potential energy interactions for the two hydrogen atoms:

- proton-electron attraction (E is negative, stabilizing)
- electron-electron repulsion (E is positive, destabilizing)
- proton-proton repulsion (E is positive, destabilizing)

The total energy of the two-atom system is a sum of these these attractive and repulsive interactions. As shown by the curve in Figure **6.1.1.2**, when the atoms are very far apart from one another, they have no interaction and the energy of the system is defined as zero. As the atoms are brought closer together, the stabilizing attraction between electrons and protons dominates. As a result, as atoms are brought together, energy is released and the system becomes more stable compared to the infinitely separated atoms. However, at very short internuclear distances, the repulsive electron–electron and proton-proton interactions dominate. Note that at a mid-distance, the diagram shows that the total potential energy of the system reaches a minimum, the point where the electrostatic repulsions and attractions are balanced. This distance, 74 pm, is called the **bond distance** (or **bond length**) of hydrogen. If the atoms are farther apart, the inward attraction toward the electron density pulls them closer together. If the atoms are closer together, their mutual repulsion pushes them apart. In practice, the atoms vibrate, as if they were connected by a spring.

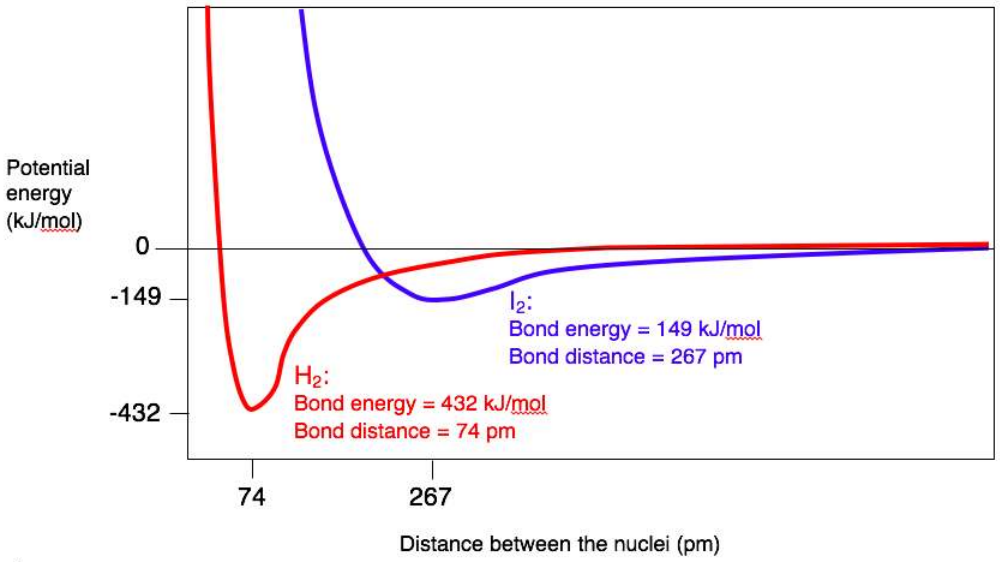
> *Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.*

The graph in Figure **6.1.1.2** also shows us that the H_2 molecule is 432 kJ/mol more stable than the unbonded atoms (which would have an energy of 0 kJ/mol). If we wanted to break a mole of H_2 into hydrogen atoms, we would need to put in 432 kJ of energy:

$$H_2(g) \rightarrow 2\ H(g) \qquad \Delta H = 432\ kJ$$

This energy is called the **bond dissociation energy** (or **bond energy**) of H_2.

Bond energies and bond distances depend on the atoms that are bonded together. A dramatic illustration of this is shown by the graph below, which compares the bond energy diagrams of H_2 and I_2.



Two Models for Covalent Bonding

There are two models that we can use to describe covalent bonding and how it produces the molecules we observe in nature

Localized Electron Model: assumes that each pair of electrons in a molecule has a specific location and function. Nonbonding electron pairs are in atomic orbitals; bonding electron pairs are found where atomic orbitals from two atoms overlap.

Delocalized Electron: assumes that each pair of electrons in a molecule occupies an orbital that encompass the entire molecule. Every molecule has a set of these molecular orbitals, which are filled in the same way that atomic orbitals are filled in a single atom.

Localized Electron Model of Covalent Bonding

The valence-bond model is essentially the Lewis structure model that you have probably encountered in your introductory chemistry class, but expanded to include some of the ideas of quantum mechanics. This model is the easier of the two to apply, so we will focus most of our attention on it.The valence-bond model, sometimes referred to as the "localized electron model" of covalent bonding, is based on the following general postulates.

1) A covalent bond is the sharing of a pair of electrons between two atoms.

We typically represent this by a Lewis structure, which shows the valence electrons as dots. You should be somewhat familiar with Lewis structures from prior coursework. Detailed instructions for drawing Lewis structures are covered in a separate section.

H:H

The Lewis structure of H_2

:Cl:Cl:

The Lewis structure of Cl_2

2) The bond forms when two atomic orbitals overlap.

For example, the bond in H_2 is formed when the 1s orbitals of the two atoms overlap.



3) Each pair of electrons that is not involved in bonding is *localized* on one atom.

In the Lewis structure of Cl_2 above, six of the seven pairs of electrons are non-bonding. Each pair is localized on one atom: three pairs on the left-hand Cl and three on the right-hand Cl.

4) The shape of a molecule is determined by the repulsion of electrons in the valence shells of the atoms.

For example, in BeF_2, the atoms line up because the two bonding electron pairs repel each other and stay on opposite sides of the Be atom.

F : Be : F	F : Be F
Better: the two electron pairs are far apart	*Worse: the two electron pairs are closer together*

Delocalized Electron Model of Covalent Bonding

The delocalized electron model model is much closer to reality than the localized electron model model. It accounts for delocalized electrons, which Lewis structures don't deal with well, and it allows us to explain some observations that Lewis structures cannot account for, such as energetic and magnetic behavior of molecules. The delocalized electron model is encompassed in Molecular Orbital Theory. This theory is based on the following assumptions:

- Every molecule has a set of orbitals.
- Each of these molecular orbitals encompasses the entire molecule.
- The rules for filling these orbitals are the same as they are for filling atomic orbitals: only 2 electrons per orbital, the lowest energy orbitals fill first, and electrons spread themselves out when they are in equal-energy orbitals.
- We can find the approximate shapes of molecular orbitals by adding wave functions for atomic orbitals.

Although more accurate, this model requires a more sophisticated mathematical treatment. We will introduce the core ideas by considering diatomic molecules.

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6.1.2: Interpreting Lewis Structures

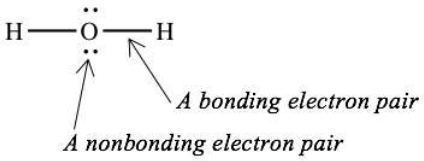
Learning Objectives

- To identify bonding and nonbonding electron pairs within a Lewis Structure.
- To identify bond order for bonds within a Lewis Structure.
- Understand the relationship between bond order, bond distance, and bond energy.
- To use electronegativities to determine bond polarity.
- To assign formal charges to each atom in a Lewis Structure.

This text assumes previous knowledge of Lewis Dot Structures. The following section will review how to draw structures, but first we will address some key Lewis Dot Structure ideas.

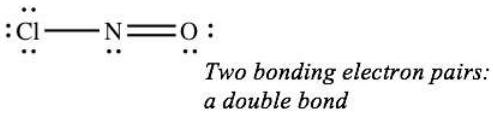
Interpreting Lewis Structures

A Lewis structure contains symbols for the elements in a molecule, connected by lines and surrounded by pairs of dots. For example, here is the Lewis structure for water, H_2O.

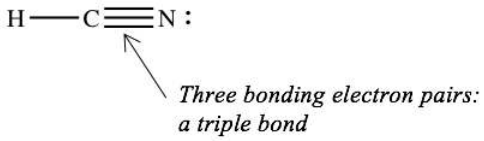


Each symbol represents the nucleus and the core electrons of the atom. Here, each "H" represents the nucleus of a hydrogen atom, and "O" represent the nucleus and the two core electrons of the oxygen atom. The dots represent nonbonding valence electrons. There are four nonbonding valence electrons on the oxygen atom. Each line represents a pair of bonding electrons, which is shared between two atoms. This is typically called a **single bond**.

When there are two lines connecting a pair of atoms, there are four bonding electrons (two pairs) between the atoms. This is called a **double bond**.



Three lines between a pair of atoms means six bonding electrons (three pairs), and is called a **triple bond**.



Bond Order, Bond Distance, and Bond Energy

The number of electron pairs in a bond is called the **bond order**.

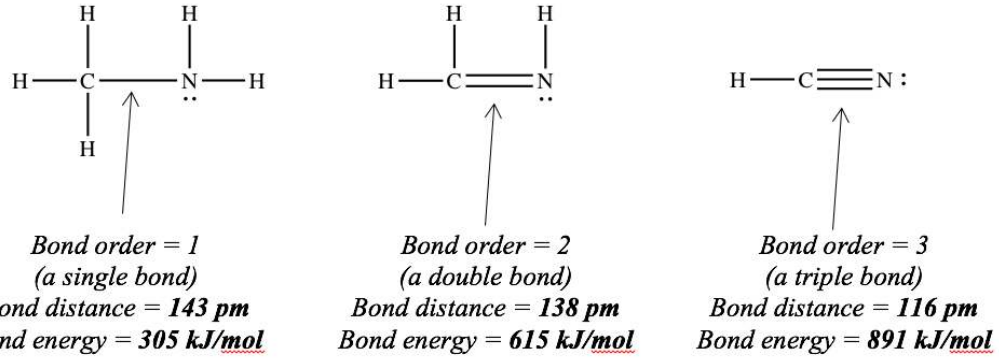
C–C	single bond	bond order = 1
C=C	double bond	bond order = 2
C≡C	triple bond	bond order = 3

The bond order is directly related to the length and strength of a bond.

Higher bond order = **stronger** bond (higher bond energy)

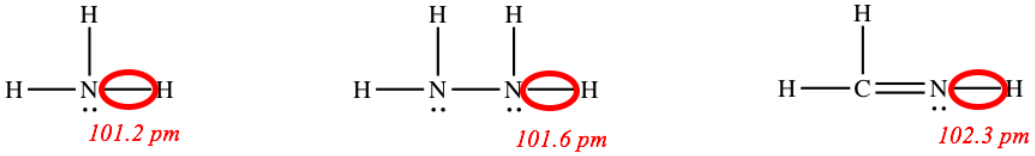
Higher bond order = **shorter** bond (smaller bond distance)

Here is an example, comparing the lengths and strengths of bonds between carbon and nitrogen.



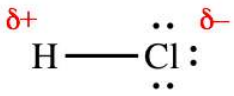
***Warning**: this only works when you compare bonds between the same pair of elements. You can safely say that a C=N double bond is shorter than a C–N single bond, but you cannot safely say that a C=N double bond is shorter than a C–H single bond. (In fact, the C–H bond is shorter!)*

The bond energy and bond distance depend on the bond order, but they normally do not depend very much on the other atoms and bonds in the molecule. For example, the circled N–H bonds in the following molecules are roughly the same length.



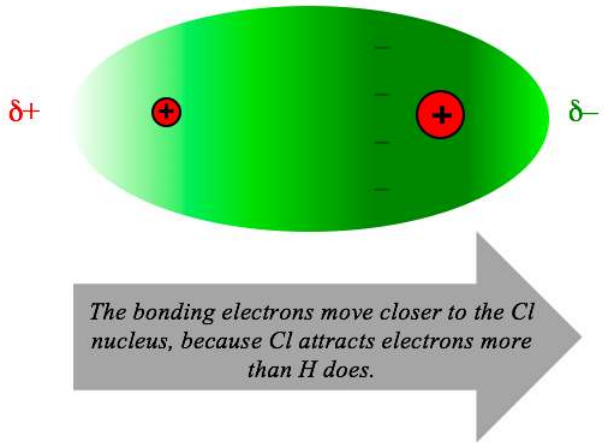
Bond Polarity

Whenever a covalent bond links atoms of different elements, the bond will be **polar**. A polar bond is one in which the atoms have unequal electrical charges. Generally, one atom will be negatively charged and the other will be positively charged. For example, the bond in HCl is polar. The hydrogen atom is positively charged and the chlorine is negatively charged. We can represent this as follows:



The symbol δ means "a little bit." We use it to show that the atoms are not ions with integer charges (+1 and –1); the hydrogen atom is slightly positive and the chlorine atom is slightly negative.

A bond is polar when the two atoms have different attractions for electrons. In the case of HCl, chlorine attracts electrons more strongly than hydrogen does. Therefore, the two bonding electrons move toward the chlorine atom, making it negatively charged (and the hydrogen positively charged).



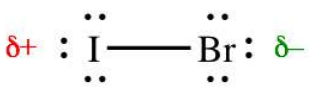
Electronegativity: determining which atom is positive and which is negative.

To figure out which atom is positively charged and which is negatively charged in a covalent bond, we use the **electronegativities** of the atoms. Electronegativity is a number that measures how strongly an atom attracts electrons, both its own electrons and those of other atoms. Here is a table that shows the electronegativities for the representative elements.

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

The elements with the lowest electronegativities are on the far left side of the table. These are elements that have weak attractions for electrons; they do not attract electrons from other atoms, and they do not hold their own valence electron(s) very tightly. These atoms tend to be positively charged when they form compounds. The elements with the highest electronegativites are in the upper right corner of the table. These are elements that have strong attractions for electrons; they can "steal" electrons from other atoms, and they hold their own valence electrons very tightly. These atoms tend to be negatively charged when they form compounds. Note that hydrogen has an intermediate electronegativity; it is quite different from the other group 1A elements (which is why many tables also show it in group 7A).

Predicting which atom is positive and which is negative in a covalent bond is easy if we know the electronegativities: *When two atoms form a covalent bond, the atom with the lower electronegativity becomes positively charged and the atom with the higher electronegativity becomes negatively charged. (Helpful mnemonic: "The atom with a higher electronegativity becomes negative.")* For example, we can use this guideline to predict the polarity of IBr. The electronegativity of I is 2.5 and that of Br is 2.8. Since 2.8 is higher than 2.5, the iodine atom is positively charged and the bromine atom is negatively charged in this molecule.



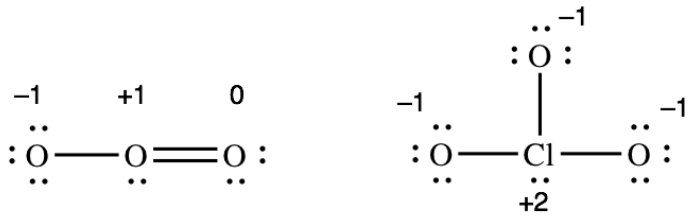
Note: in formulas of compounds involving covalent bonds, the atom with the lowest electronegativity is normally written first (so we write IBr, not BrI).

Formal charges

In general, compounds that are built entirely from nonmetals are not ionic. The atoms are held together by covalent bonds. For example, HCl is H–Cl, not H^+ Cl^-. The atoms may have weak electrical charges, because the bonds that link them are polar, but there are no ions present.

However, for some purposes, it is useful to carry out a sort of "electron book-keeping" and assign “make-believe” charges to the atoms in a covalently-bonded compound. For example, assigning charges to atoms can help us to predict which of two possible arrangements of atoms is more stable. For example, we can predict that the arrangement H–C–N is more stable than the arrangement H–N–C for the compound HCN. In addition, these charges help us to understand and balance oxidation-reduction reactions, in which one or more atoms change charges. (You will learn about these reactions in Chem 101B.)

The charges that we assign to atoms in a covalently-bonded molecule are called **formal charges**. Every atom in a molecule or polyatomic ion has a formal charge (which could be zero). For example, here are the formal charges in O_3 (a molecule) and ClO_3^- (a polyatomic ion):



We will look at how to assign formal charges in a moment, but first, note that **the formal charges must add up to the overall charge on the molecule or ion**.

For O_3, -1 + 1 + 0 = **0** (which matches the overall charge on O_3)

For ClO_3^{2-}, -1 + 2 + -1 + -1 = **-1** (which matches the overall charge on ClO_3^-)

Assigning Formal Charges

To assign formal charges to each of the atoms in any molecule or polyatomic ion, you must compare number valence electrons that each atom contributes or "brings" to the molecule to the number of electrons that the atom "owns" in the molecule.

(1) The number of electrons which an atom "brings" to the molecule is determined by its position on the periodic table. The number of electrons it "brings" is equatl to the valence electrons on the neutral atom.

(2) The number of electrons which an atom "owns" in determined based on the following:

* Non-bonding electrons "belong" to the atom on which they are located.

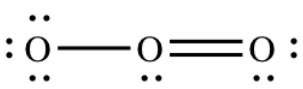
* Bonding electrons must be "split" between the two bond atoms involved in the bond (they are sharing after all...)

The formal charge for an atom is:

(number of electrons the atom brings to the molecule) – (number of electrons the atom actually owns in the molecule)

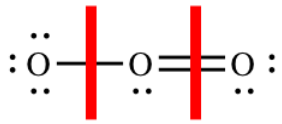
Here are two illustrations:

1) Formal charges on O_3 (ozone):



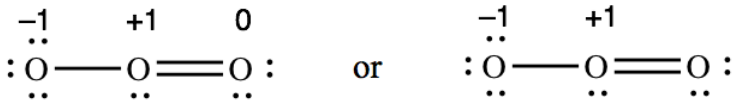
For each atom in the molecule, we must determine how many electrons it "brings" to the molecule and how many electrons it "owns" in the molecule. Oxygen is in group 6A, so each of the oxygen atoms will bring six valence electrons to the molecule. To

determine the number of electrons each atom "owns" you follow the guidelines above, adding the non-bonding electrons and half of the bonding electrons. The red lines show where we must "split" the bonding electrons:



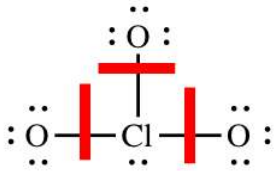
	Left oxygen atom	Center oxygen atom	Right oxygen atom
number of electrons the atom brings to the molecule	6	6	6
number of electrons the atom actually owns in the molecule	7 *(six non-bonding, one bonding)*	5 *(two non-bonding, three bonding)*	6 *(four non-bonding, two bonding)*
formal charge = *"brings" – "owns"*	-1	+1	0

Formal charges are usually written next to the atoms in the original Lewis structure. We often omit the zeroes and just write the nonzero formal charges.



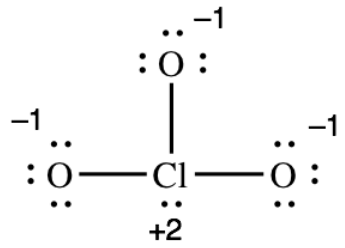
2) Formal charges on ClO_3^- (chlorate ion):

For each atom in the molecule, we must determine how many electrons it "brings" to the molecule and how many electrons it "owns" in the molecule. Oxygen is in group 6A, so each of the oxygen atoms will bring six valence electrons to the molecule. Chlorine is in group 7A and bring seven valence electrons to the molecule. To determine the number of electrons each atom "owns" you follow the guidelines above, adding the non-bonding electrons and half of the bonding electrons. The red lines show where we must "split" the bonding electrons:



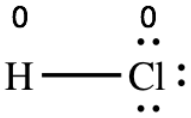
Formal charge analysis of the atoms in ClO- ion

	Chlorine atom	Left oxygen atom	Top oxygen atom	Right oxygen atom
number of electrons the atom brings to the molecule	7	6	6	6
number of electrons the atom actually owns in the molecule	5 *(two non-bonding, three bonding)*	7 *(six non-bonding, one bonding)*	7 *(six non-bonding, one bonding)*	7 *(six non-bonding, one bonding)*
formal charge = *"brings" – "owns"*	+2	-1	-1	-1

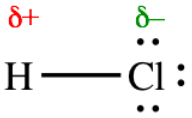


Lewis structure of IBr showing partial positive charge on I and patial negative charge on Br

Note the difference between formal charges and partial charges based on bond polarity. Formal charges are artificial charges that we calculate by breaking Lewis structures apart in a sort of electron book-keeping. We can calculate them, but they are not the true charges on the atoms. Bond polarities give us a rough idea of the true charges on atoms in a molecule, but we cannot calculate numbers. For example, the formal charges on both atoms in HCl are zero, but we know that the true charges are not zero, because the electronegativities are different.



formal charges



actual charges based on bond polarity

Formal charges will prove useful tools in future sections, but for now, just focus on how to correctly calculate them.

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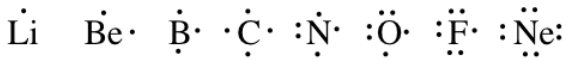
6.1.3: Drawing Lewis Structures

Learning Objectives

- To draw Lewis Structures for molecules and polyatomic ions with one central atom.

Introduction to Lewis structures

A Lewis structure is a way to show how atoms share electrons when they form a molecule. Lewis structures show all of the valence electrons in an atom or molecule. *The valence electrons are the electrons in the outermost shell. For representative elements, the number of valence electrons equals the group number on the periodic table.* To draw the Lewis structure of an atom, write the symbol of the atom and draw dots around it to represent the valence electrons.



Note that hydrogen is often shown in both group 1A and group 7A, but it has one valence electron – never seven. Also, helium is shown in group 8A, but it only has two valence electrons.

Representing a Covalent Bond Using Lewis Structures

Nonmetals can form a chemical bond by sharing two electrons. Each atom contributes one electron to the bond. For example, two hydrogen atoms can form a bond, producing a molecule of H_2. Using Lewis structures, we can represent this as follows:



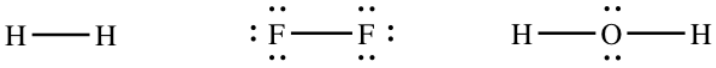
Two fluorine atoms can form a molecule of F_2 in the same fashion. Note that each atom must contribute one electron to the bond.



Atoms can form more than one bond. In a water molecule, an oxygen atom forms two bonds, one to each hydrogen atom.



Chemists normally represent a bond using a line instead of two dots. The structures of H_2, F_2, and H_2O would usually be drawn as follows:



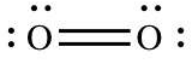
Only the bonding electrons are shown using lines. Nonbonding electrons are always shown using dots.

Multiple Bonds

The bonds on the previous section are called single bonds. Each bond contains two electrons (one bonding pair). A pair of atoms can also share four electrons or six electrons. If the atoms share four electrons, the bond is called a double bond. For example, the bond in O_2 is a double bond.



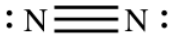
A double bond is normally depicted with two parallel lines.



If the atoms share six electrons, the bond is called a triple bond. Triple bonds are rather rare, but the bond in N_2 is a triple bond.



A triple bond is depicted with three parallel lines.

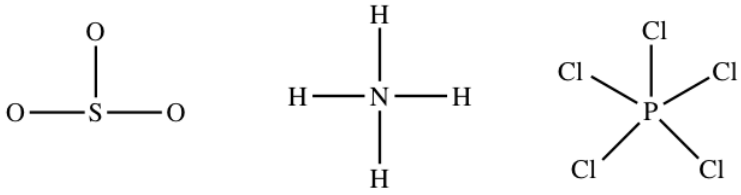


Drawing Lewis structures for molecules with one central atom: two rules

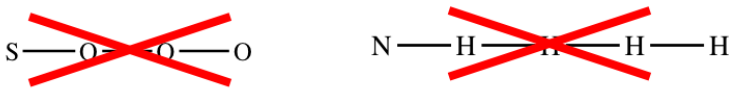
In Chem 101A, we will focus on drawing Lewis structures of molecules and polyatomic ions that have one central atom with several other atoms attached to it. Such molecules are very common, and they provide a foundation for understanding structures of more complex molecules. To begin, you must know two essential rules for drawing Lewis structures.

Rule 1: *In any molecule or ion with the general formula AB_n, the unique atom (A) is in the center and all of the B atoms are attached to A.*

For example, the basic arrangements of the atoms in SO_3, NH_4^+, and PCl_5 are:

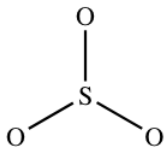


Do not ever draw a structure like the ones below!



Rule 2: *Lewis structures are not intended to show the actual shape of the molecule; they only show which atoms are bonded to each other.*

None of the molecules above actually look like the structures here. For example, the actual shape of SO_3 is:



Drawing Lewis structures for molecules with one central atom: steps to success

The following procedure will give you the correct Lewis structure for any molecule or polyatomic ion that has one central atom.

Step 1: Figure out how many electrons the molecule must have, based on the number of valence electrons in each atom. When drawing the structure of an ion, be sure to add/subtract electrons to account for the charge.

Step 2: Connect the atoms to each other with single bonds to form a "skeleton structure."

Step 3: Starting with the outer atoms first, add the remaining valence electrons, giving each atom an octet. (Exception: do not add electrons to hydrogen atoms.)

- **If there are too few electrons** to give all atoms the necessary octets, then make double or triple bonds. (Avoid double bonds to halogens, if possible.)
- **If there are "extra" electrons** remaining after all atoms have octets, then add them as lone pairs to the central bonding atom. Note: if a central atom must accommodate more than 8 electrons around it, we say that this central atom has an "expanded octet". Expanded octets are fairly common with elements in the 3rd row and below, and it is okay to violate the octet rule, if necessary, for these larger atoms.

Step 4: Check that your structure is valid. A valid structure must have the correct number of valence electrons and obey the octet rule where necessary. Note: there may be more than one valid Lewis Structure.

- **Are the correct number of valence electrons shown?** The electron count in your final structure must match the count from step 1.
- **Do all atoms have an octet?** (If not, are they one of the exceptions to the rule? See below.)

WARNING: exceptions to the octet rule!

The octet rule dictates much of the bonding patterns in chemical structure. However, there are many exceptions. You will need to know when it is okay to break the octet rule.

1. Hydrogen must have a "duet" (two electrons). Do not give hydrogen an octet.
2. Boron often has a "sextet" (six electrons). If necessary, boron can have an octet.
3. Elements in the 3rd row and below can accommodate more than an octet, if necessary.

Example: drawing the Lewis structure of CO_3^{2-}

Step 1) Total the valence electrons.

Carbon has 4 valence electrons

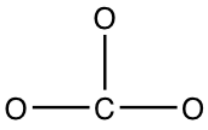
Each oxygen has 6 valence electrons

The -2 charge means that there are 2 extra electrons

Total: 4 + (3 × 6) + 2 = 24 electrons

The final answer MUST have this number of electrons!!!

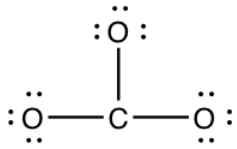
Step 2) Draw the "skeleton structure".



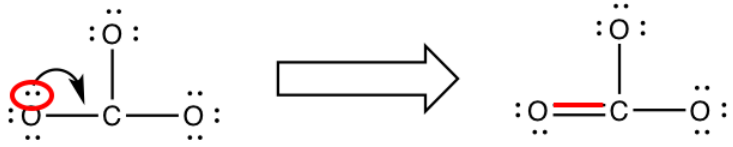
Step 3) Add remaining valence electrons, starting with the outer atoms first, giving all atoms an octet (except H).

The outer atoms are the oxygen atoms here. Each outer atom needs three electron pairs, since it already has one bonding pair.

(1 line = 2 electrons)



In the above structure, the outer atoms now all have an octet, but note that the central atom does not!! Unfortunately, we have run out of electrons (we only had 24!!). Since we do not have any additional electrons available, we will ***create an extra bond by changing one of the nonbonding pairs into a bonding pair.***



We convert the nonbonding pair in the circle...

...into a bond.

Notice that this step does not change the total number of electrons in our structure. It just moves 2 electrons to a different location.

Step 4) Check if the structure is valid.

a) Are the correct number of valence electrons shown? The electron count in your final structure must match the count from step 1.

This structure has 24 electrons.

3 lines = 6 bonding electrons

18 dots = 18 nonbonding electrons

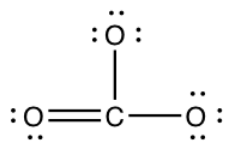
total = 24 electrons

Does this match the count you got in step 1?

CO_3^{2-}: should have 24 electrons *(from step 1)* and our structure has 24 electrons – check! It MATCHES!

b) Do all atoms have an octet? (If not, are they one of the exceptions to the rule?)

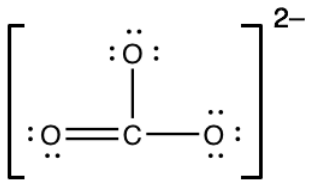
Yes, all atoms in this structure have an octet.



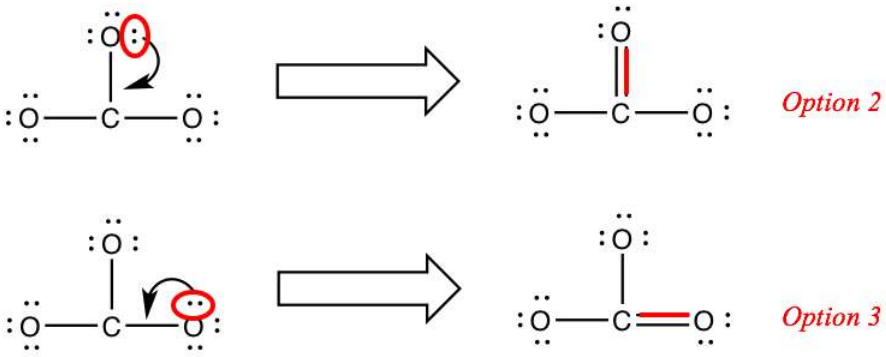
The carbon now has 8 electrons around it (4 lines = 8 electrons), so we stop here!

This is the correct structure for carbonate ion.

Chemists often draw square brackets around the structure of a polyatomic ion and write the charge outside the brackets, like this:



Note: we could have put the double bond in two other locations. Any of the three options is fine; you only need to draw one of them.



Option 2

Option 3

(If you're wondering "what about resonance??"… we'll get to that later on.)

Example: Drawing Lewis structures for BF_3, PF_3 and BrF_3

Next, we'll look at three molecules side-by-side. The molecules are BF_3, PF_3, and BrF_3, all of which have a central atom bonded to three fluorine atoms.

Step 1) Figure out how many electrons each molecule must have.

BF_3: 3 + 7 + 7 + 7 = 24 electrons

PF_3: 5 + 7 + 7 + 7 = 26 electrons

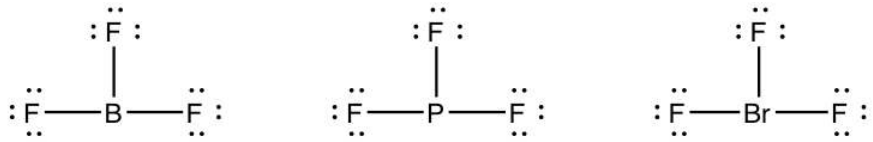
BrF_3: 7 + 7 + 7 + 7 = 28 electrons

The final answers MUST have these numbers of electrons!!!

Step 2) Draw a "skeleton structure".

Step 3) Add the remaining electrons, starting with the outer atoms, to complete their octets.

Each outer atom needs three electron pairs.



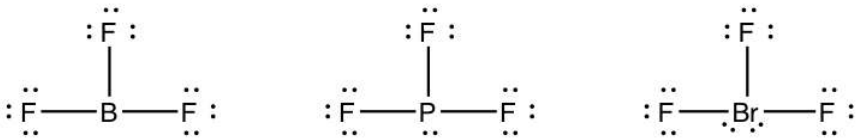
The outer atoms now have octets. Let's pause here...

BF_3: Our structure has 24 electrons, so we've added all the valence electrons *(from step 1)*

PF_3: Our structure has 24 electrons, but we know it should have 26 electrons *(from step 1)*, so WE STILL NEED TO ADD 2 MORE ELECTRONS

BrF_3: Our structure has 24 electrons, but we know it should have 28 electrons *(from step 1)*, so WE STILL NEED TO ADD 4 MORE ELECTRONS

These "extra" electrons should be added to the central atom, as pairs:



We added two electrons to the phosphorus atom.

We added four electrons to the bromine atom.

Step 4) Check if the structure is valid.

BF_3: *a) Our structure has 24 electrons (6 bonding electrons and 18 nonbonding electrons), matching the count in step 1!*

b) The fluorine atoms all have an octet. Check! The boron atom does not have an octet, but boron is one of the exceptions and is fine with a sextet. So, check!

PF_3: *a) Our structure has 26 electrons (6 bonding electrons and 20 nonbonding electrons), matching the count in step 1!*

b) All atoms have an octet. Check!

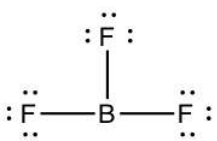
BrF_3: *a) Our structure has 28 electrons (6 bonding electrons and 22 nonbonding electrons), matching the count in step 1!*

b) The fluorine atoms all have an octet. Check! The bromine has more than an octet, but bromine is in period 4 and can accommodate an expanded octet. So, check!

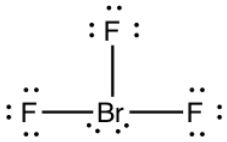
Breaking the Octet Rule is common

The central atom in a structure often violates the octet rule. Electron-deficient atoms are rare, but expanded octets are fairly common with elements in the 3rd row and beyond.

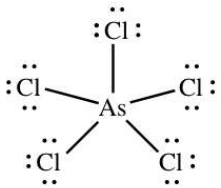
In BF_3, the central atom only has 6 electrons around it. We say that the boron atom is ***electron deficient.***



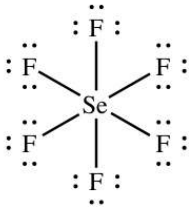
In BrF_3, the central atom has 10 electrons around it. We say that the bromine atom has an ***expanded octet.***



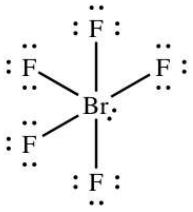
Note that it is also quite common for the central atom to make more than four bonds. Here are a couple of examples:



$AsCl_5$
(As has 5 bonds)



SeF_6
(Se has 6 bonds)

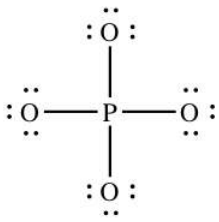


BrF_5
(Br has 5 bonds plus a nonbonding pair)

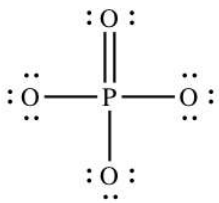
Don't panic if you see such molecules. Just follow the rules for drawing Lewis structures, and you'll get them right! **However, you must note that outer atoms never violate the octet rule.**

Using formal charges to determine how many bonds to make, a different perspective...

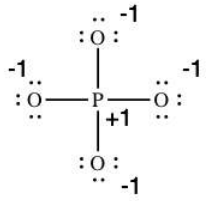
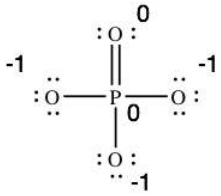
If we draw the Lewis structure for PO_4^{3-} ion using the rules you've seen earlier, we come up with the structure below. It has the correct number of electrons (32), and every atom satisfies the octet rule.



However, many textbooks (and websites) insist that the structure below is a better one, even though the phosphorus atom has ten electrons around it:



The first structure follows the rules for drawing structures. So why do chemists add a double bond? To understand, we need the formal charges on the atoms in each structure…

Many chemists prefer the second structure because it gives us a couple of zeroes. However, the phosphorus atom in the second structure violates the octet rule. So which structure is best?? The answer is that **either structure is legitimate**. Both structures give us all of the information we need about phosphate ion; they allow us to predict the shape of the molecule, the angles between the bonds, and whether the molecule is polar.

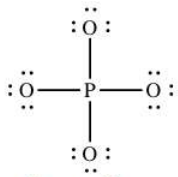
So which structure should YOU draw on a test? Be sure to check with your instructor, but most will accept either one. However, *the first structure is easier to figure out*, because it's the structure you produce when you follow the provided rules. The second structure requires more work. Therefore, we recommend that when you draw a structure that satisfies the octet rule, you stop there without adding more bonds.

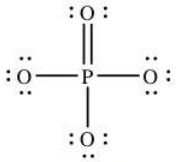
WARNING: Some students come to Chem 101A having been taught to draw Lewis structures with extra double bonds.

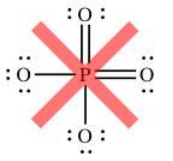
If you're familiar with Lewis structures and you like the extra bonds… congratulations! You have less to learn – you already know all of this stuff.

BUT…

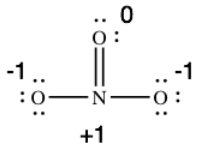
If you draw structures with extra bonds, they have to be correct. For example, a structure for phosphate that has <u>two</u> double bonds is not acceptable.


Acceptable


Acceptable


Not acceptable

Also, a structure for nitrate ion (NO_3^-) that has two double bonds is not acceptable, even though it gives you more zeroes. The structure with one double bond is the only acceptable one.


Acceptable


Not acceptable

If you don't know why the structures I've labeled "unacceptable" are not allowed, don't risk losing points by adding extra bonds when the central atom already has eight electrons.

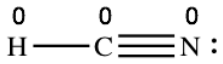
Using formal charges to evaluate which is the best central atom...

Generally, you are told which atom is the central bonding atom in the molecule. However, if it is unclear, or if you are asked to decide which atom is central, formal charges can be used to decide. The following is an example.

Example: calculating the formal charges in HCN and HNC

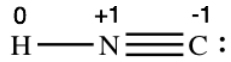
For the arrangement HCN, the Lewis structure: H–C≡N:

The formal charges work out as follows:



For the arrangement HNC, the Lewis structure: H–N≡C:

The formal charges work out as follows:



Both Lewis structures have a *net* formal charge of zero, but note that the formal charges on the first structure are all zero! Thus the first Lewis structure is predicted to be more stable, and it is, in fact, the structure observed experimentally. In general, the closer the formal charges are to zero, the more stable the structure. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a book-keeping method for predicting the most stable Lewis structure for a compound.

Summary

References

Contributors and Attributions

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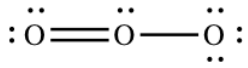
6.1.4: Resonance Lewis Structures

Learning Objectives

- Use resonance structures to show electron delocalization.
- Use formal charges to determine major and minor resonance contributors.

Sometimes one Lewis Structure is not Enough

Some molecules or ions cannot be adequately described by a single Lewis structure. For example, drawing one Lewis structure for ozone (O_3) gives us a misleading picture of the actual bonding in the molecule. If we draw a Lewis structure for O_3 (ozone), we get this:



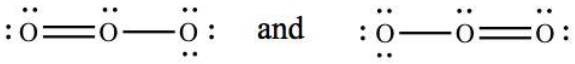
This structure predicts that the two bonds are different lengths and strengths, because double bonds are shorter and stronger than single bonds. However, this prediction in incorrect; the two bonds in O_3 are actually *identical* in length and strength.

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 resonance contributors). The basic concept of resonance theory is the following:

Whenever you can draw two or more equivalent Lewis structures for a molecule, the actual molecule behaves like the average of the possible structures.

Applying resonance theory to O_3

Let's apply resonance theory to O_3. For this molecule, we can draw two equivalent structures, as shown below:



Using resonance theory, we predict that the true structure of ozone is the average of these two structures. *But how do you take the average of two chemical structures??* When we take the average of two structures, we are really taking the average of two things: the bond orders and the formal charges.

Let's begin with bond orders. We start by looking at the order of the left-hand bond in each structure. *(Remember that the bond order is the number of electron pairs between two atoms. For a single bond, the bond order is 1; for a double bond, it's 2; and for a triple bond, it's 3.)*



One structure tells us that this is a double bond, while the other tells us that it's a single bond. **The actual order of the left-hand bond should be the average of these two numbers, which is 1.5.** Next, we focus on the right-hand bond. Again, one structure tells us that it is a double bond, while the other tells us that it's a single bond.



The actual order of the right-hand bond should be the average of these two numbers, which is also 1.5. Based on resonance theory, the molecule should have two equal bonds, each of which has an order of 1.5. We can depict this using lines to represent partial

bonds:



When we want to show that we must use resonance theory to understand the behavior of a molecule, we draw all of the legitimate structures and use double-sided arrows to mean “take the average of these.”

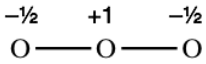


The double-sided arrow always means “take the average”!

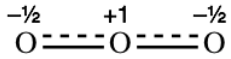
We can also use resonance theory to refine our understanding of formal charges. The formal charges in each structure are shown below.



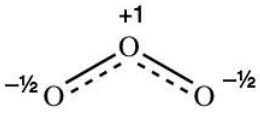
In resonance theory, we take the average of the formal charges on each atom. For the central atom, the formal charge is +1 in both structures, and the average of +1 and +1 is +1. For the left-hand atom, we are finding the average of 0 and –1, which is –½ . For the right-hand atom, we are finding the average of –1 and 0, which is also –½ . Therefore, resonance theory gives us the following charges:



In ozone, then, the central atom is positively charged, and the outer atoms are negatively charged (and have equal charges). The overall picture of ozone that we end up with is…

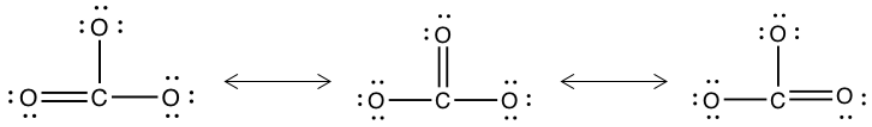


Or if we have used the Valence Shell Electron Pair Repulsion Theory (VSEPR) to determine the three-dimensional shape:

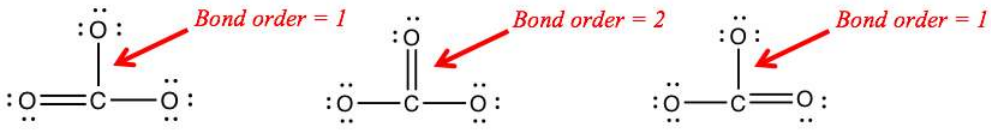


Applying resonance theory to CO_3^{2-}

The carbonate ion is an example of a molecule for which we can draw three equivalent structures. Each structure has one double bond and two single bonds, suggesting that one of the bonds is shorter than the other two. However, since the structures are equivalent, we must take the average of the three to get an accurate picture of carbonate.



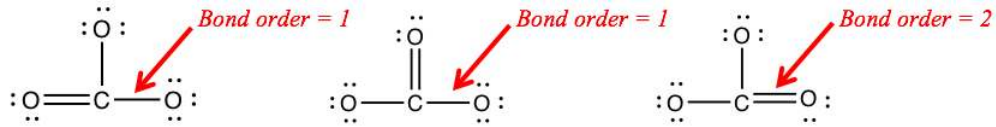
Once again, we have to consider one bond at a time. Let’s start with the vertical bond:



The true order of this bond is the average of these three numbers:

$(1 + 2 + 1) \div 3 = {}^{4}/_{3}$

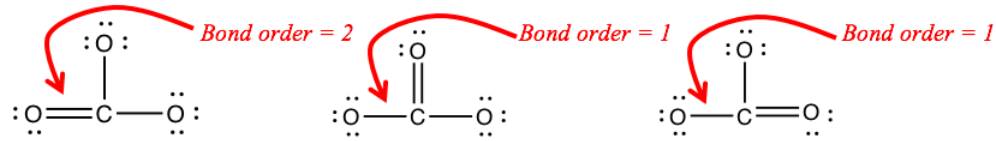
Next, let's do the right-hand bond:



The true order of this bond is the average of these three numbers:

$(1 + 1 + 2) \div 3 = {}^{4}/_{3}$ *(the same as the vertical bond)*

Finally, we do the left-hand bond:

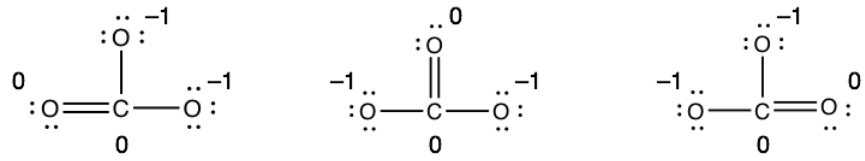


The true order of this bond is the average of these three numbers:

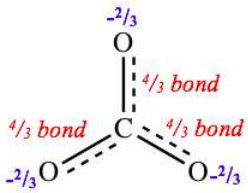
$(2 + 1 + 1) \div 3 = {}^{4}/_{3}$ *(the same as the other two bonds)*

Using the resonance theory, we predict that the three bonds in the carbonate ion should be identical, with a bond order of ${}^{4}/_{3}$. In fact, this is correct: the three bonds in the carbonate ion really are the same length. Also, these three bonds are shorter than a typical C–O single bond, and they are longer than a typical C=O double bond.

For the formal charges, we first work out the formal charge on each atom in each structure.



Then we look at each atom. The central carbon atom has a charge of zero in all structures, so its charge is zero when we take the average. For the left-hand oxygen, the charge is zero in the first structure and –1 in the other two; the average is $(0 + -1 + -1) \div 3 = -{}^{2}/_{3}$. The other two oxygen atoms give the same result, so all three oxygen atoms have a charge of $-{}^{2}/_{3}$. The overall bonding picture that results is:



The three dimensional shape is that predicted by Valence Shell Electron Repulsion Theory.

Example 6.1.4.1: 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

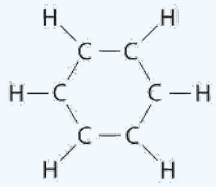
Asked for: resonance structures

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.

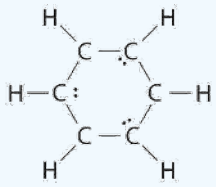
Solution:

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:



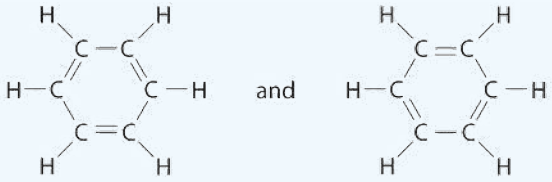
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

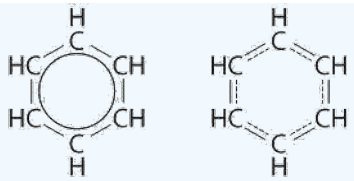


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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:

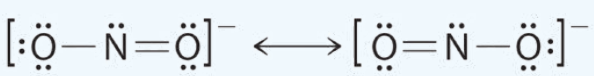


Benzene

Exercise 6.1.4.1: 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.

What resonance is NOT…

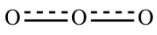
There are three common misunderstandings about resonance theory. Be careful not to fall into these traps!

1) **Resonance does <u>not</u> mean that the molecule goes back and forth between the structures.**

Ozone does not go back and forth between the two structures we can draw. It never has one short bond and one long bond.

Ozone never looks like this: O=O—O

Ozone never looks like this either: O—O=O

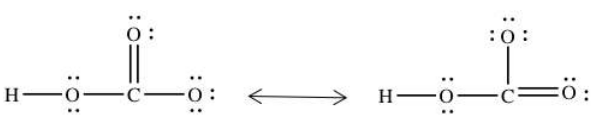
Instead, it always looks like this: 

2) **In resonance, you can only move electrons. Never move atoms.**

For example, the following two structures are <u>not</u> legitimate resonance structures, because we have moved the hydrogen atom. The true structure of HCO_3^- is <u>not</u> the average of these two structures.

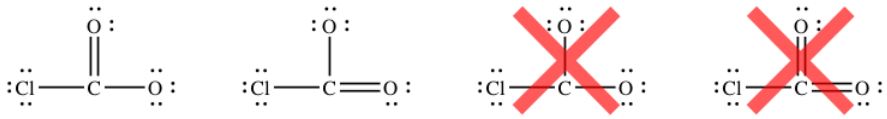


However, the two structures below <u>are</u> legitimate resonance structures, and we would need to average them to find the true structure of bicarbonate ion.

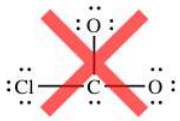


3) **Resonance structures cannot disobey the octet rule.**

In the example below (the chloroformate ion, $ClCO_2^-$), the first two structures are legitimate, but the third and fourth structures violate the octet rule (the central atom has only six electrons in structure #3, and it has ten electrons in structure #4).

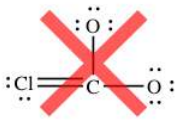


The structure below is also incorrect, but for a different reason. It obeys the octet rule, but HCO_2^- must have a total of 18 electrons, and the structure below has 20. This would be the structure of HCO_2^{3-}.



In general, all legitimate resonance structures for a given molecule will have the same number of double bonds.

Finally, the structure below is also incorrect, but for yet another reason: chlorine is in group 7A, and the group 7A elements cannot form double bonds.



What if resonance structures are not equivalent?

Sometimes, it's possible to draw two legitimate Lewis structures for the same arrangement of atoms without the structures being equivalent. For example, consider the following two structures for nitrous acid, HNO_2.

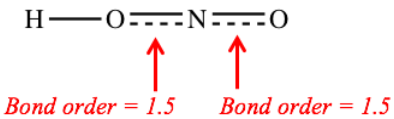


Both of these structures obey the rules for drawing Lewis structures; they have the correct number of electrons, and all atoms (other than H) obey the octet rule. In addition, we have not moved any atoms around; both structures have the arrangement H–O–N–O. However, the structures are **not equivalent**. In the first structure, the two oxygen atoms have the bonding patterns –O– and =O. In the second structure, the two oxygen atoms have the bonding patterns –O= and –O. ***When two resonance structures are not equivalent, the real molecule will most closely resemble the structure that has more atoms with zero formal charge.*** Working out formal charges for the atoms in these structures, we get:

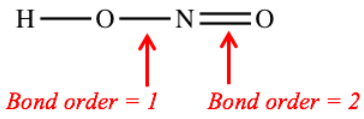


In the left-hand structure, all formal charges are zero, but the right-hand structure has two non-zero formal charges. Therefore, **the true structure of HNO_2 looks more like the structure on the left**. To envision this, we can start by drawing the average of the two structures. Then, the true structure will be somewhere between the average and the left-hand structure.

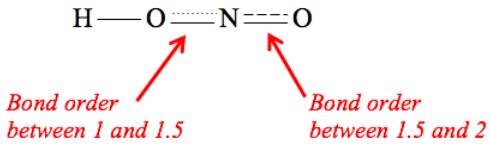
The average of the two structures would look like this (considering the bond orders only):



The left-hand structure from the previous page looked like this:

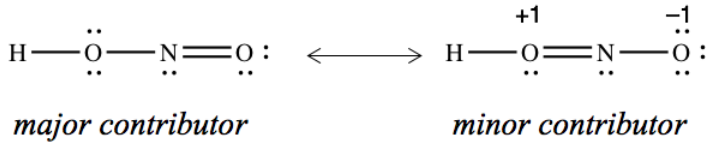


The real structure of HNO_2 lies somewhere between these two.

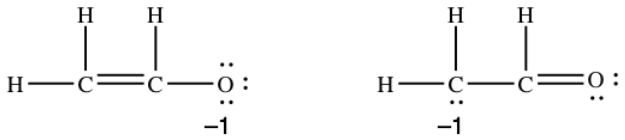


The actual bond distances in this molecule are 146 pm for the left-hand N–O bond and 120 pm for the right-hand N–O bond, agreeing with our picture.

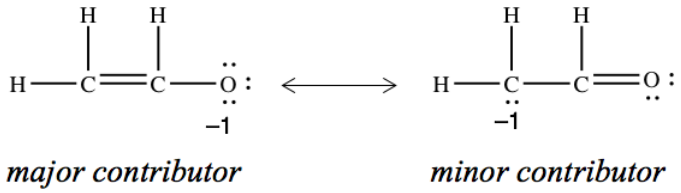
Instead of drawing a structure with dashed lines to represent partial bonds, chemists normally draw the resonance structures and label them as a "major contributor" or a "minor contributor." The major contributor is the structure that has the most zeroes; the actual molecule will look most like the major contributor.



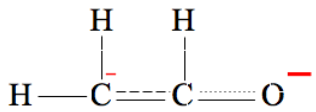
We also encounter situations where the formal charges are the same in both structures, but the atoms that hold the non-zero formal charges are different. The $C_2H_3O^-$ ion is an example. Here are the two possible resonance structures for this ion, with the non-zero formal charges included.



Both structures have five atoms with zero formal charge and one atom with a formal charge of –1. In such cases, **the true structure resembles the structure that has the negative charge on the atom with the higher electronegativity (or the positive charge on the atom with the lower electronegativity).** Oxygen has a higher electronegativity than carbon (3.5 versus 2.5), so the left-hand structure is the major contributor. We can represent this as follows:



Here is a sketch that might help you envision what the real molecule would look like. The negative charges are included; the larger minus sign means that there is a larger negative charge on the oxygen atom.



Example 6.1.4.3: 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

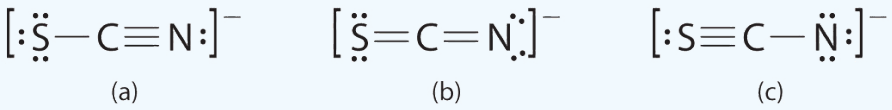
Asked for: Lewis electron structures, formal charges, and preferred arrangement

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 ???.
C. Predict which structure is the major contributor 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:



(a) (b) (c)

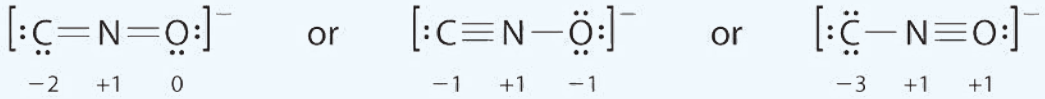
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, 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 6.1.4.1: 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

Resonance occurs when we can draw two or more legitimate Lewis structures for the same molecule.

Resonance only occurs when a molecule has at least one double bond. Molecules with only single bonds never show resonance.

Resonance structures must all have the correct number of electrons and must all obey the octet rule.

All resonance structures must have the atoms in the same positions. (“Don’t move the letters – just move dots and lines.”)

All resonance structures for a given molecule have the same number of double bonds.

If all resonance structures are equivalent, the true molecule is the average of the resonance structures.

If the resonance structures are not equivalent, the true molecule looks more like…

· …the structure with the most zeroes (formal charges), or…

· …the molecule with the negative charge on the atom with the highest electronegativity and/or the positive charge on the atom with the lowest electronegativity.

Contributors and Attributions

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6.1.5: Strength of Covalent Bonds

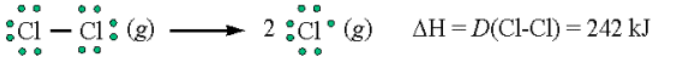
Learning Objectives

- 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.

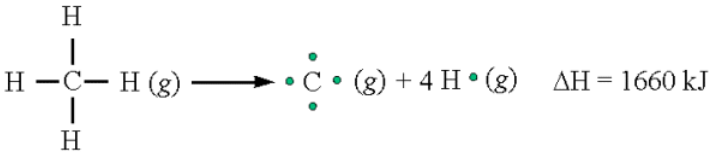
Bond Dissociation Energy

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. Table **6.1.5.1** lists the average values for some commonly encountered bonds. Note that bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation.)

Table **6.1.5.1**: 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	614
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	839
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	391	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	O=O	495
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	N=O	607
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	941
H–Cl	428	C–I	213			S–Br	218	Br–I	175	C≡N	891
H–Br	362	Si–Si	222					I–I	149	C≡O	1072
H–I	295	Si–O	452							C=O	745
										C=O (in CO_2)	799

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).

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 **6.1.5.1** 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 **6.1.5.1**).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure **6.1.5.1**. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$Cl–Cl > Br–Br > F–F > I–I \tag{6.1.5.1}$$

   Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.
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.

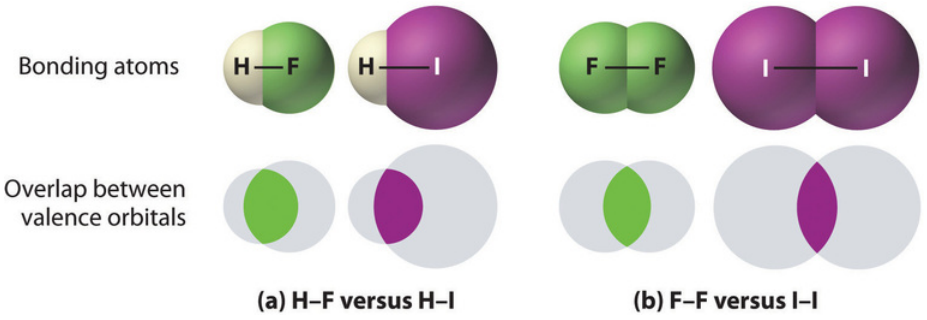


***Figure* 6.1.5.1**: *The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space relative to the size of the bonded atom decreases; that is, the percentage of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.*

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion. In 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 strength* ***increases*** *as bond order* ***increases.***
>
> *Bond distance* ***decreases****, as bond order* ***increases****.*

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 **6.1.5.2**); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table **6.1.5.1** 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 **6.1.5.2**: Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

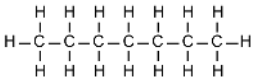
Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

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 ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{6.1.5.2}$$

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 *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. Note: *n*-heptane is a chain of seven carbon atoms, with hydrogen atoms bonded to each carbon:



This reaction of *n*-heptane is one reaction that occurs during the combustion of gasoline:

$$\mathrm{C_7H_{16}\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g)} \tag{6.1.5.3}$$

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	495 × 11 = 5445		**Total** = 18,530
	Total = 14,097		

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$

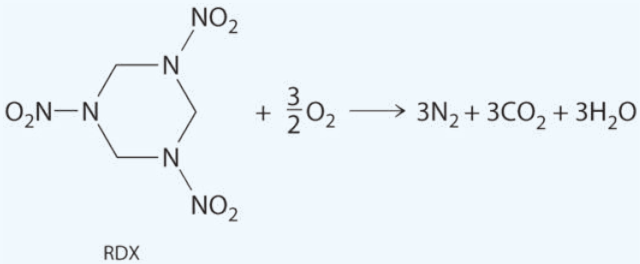
$$\Delta H_{rxn} \approx 14,097 kJ/mol - 18,530 kJ/mol = -4433 kJ/mol$$

For the above example, the energy required to break the bonds in the reactant molecules (14,097 kJ/mol) was less than the energy released upon formation of the bonds in the products (18,530 kJ/mol)! The difference is about 4433 kJ/mol, meaning that ΔH_{rxn} is approximately −4433 kJ/mol. 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 ($\Delta H_{rxn} = -4817 kJ/mol$), 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. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

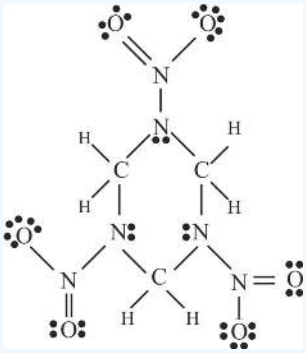
Example 6.1.5.1: Explosives

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated in the presence of oxygen, it produces gaseous products N_2, CO_2, H_2O) and heat according to the following reaction.



RDX

The RDX molecule shown above is a simplified version. Here is the complete structure.



Use the approximate bond energies in Table **6.1.5.1** to estimate the ΔH_{rxn} per mole of RDX.

Given: chemical reaction, structure of reactant, and Table **6.1.5.1**.

Asked for: ΔH_{rxn} per mole

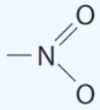
Strategy:

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 **6.1.5.1** 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		

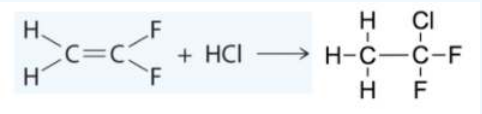
B From Equation **6.1.5.1**, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

Exercise 6.1.5.1: Freon

1-Chloro-1,1-difluoroethane (**HCFC-142b**) is a haloalkane with the chemical formula CH_3CClF_2. It belongs to the hydrochlorofluorocarbon (HCFC) family of man-made compounds that contribute significantly to both ozone depletion and global warming when released into the environment. It is primarily used as a refrigerant where it is also known as R-142b and by trade names including Freon-142b.[2] The compound *HCFC-142b* is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons traditionally used in refrigeration systems. *HCFC-142b* can be prepared by adding HCl to 1,1-difluoroethylene:



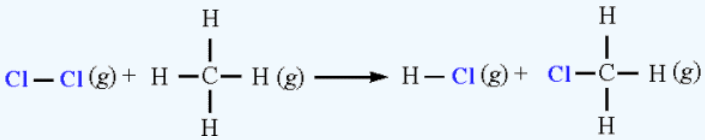
Use tabulated bond energies (Table **6.1.5.1**) to calculate ΔH_{rxn} for the preparation of *HCFC-142b*.

Answer

−42 kJ/mol

Example 6.1.5.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation ???, which requires tabulating bonds broken and formed.

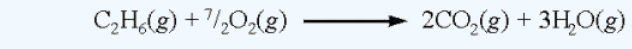
- **Bonds broken**: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed**: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

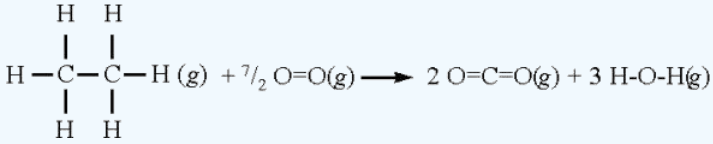
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 6.1.5.3: Combustion of Ethane

What is the enthalpy of reaction for the combustion of 1 mol of ethane?





Solution

We use Equation ???, 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.

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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6.1.6: The VSEPR Model

Learning Objectives

- To use the VSEPR model to predict molecular geometries.

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 premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

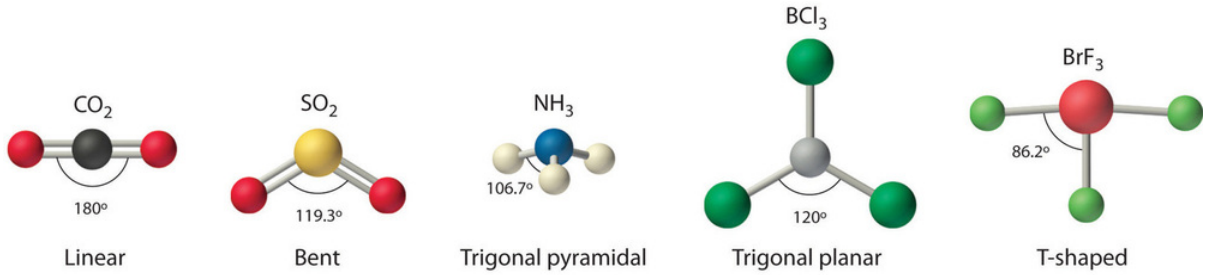


Figure* 6.1.6.1*: *Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms*

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on 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 Figures 6.1.6.1 and 6.1.6.2.

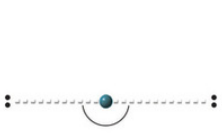
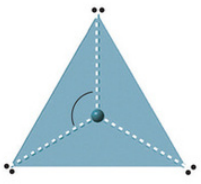
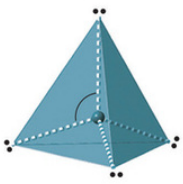
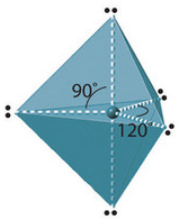
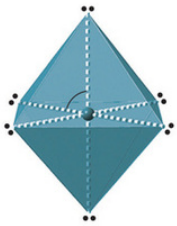
Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
					
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

***Figure* 6.1.6.2:** *Electron 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.

VESPR Produce to predict Molecular geometry

This VESPR 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 **6.1.6.2** and Figure **6.1.6.3**, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

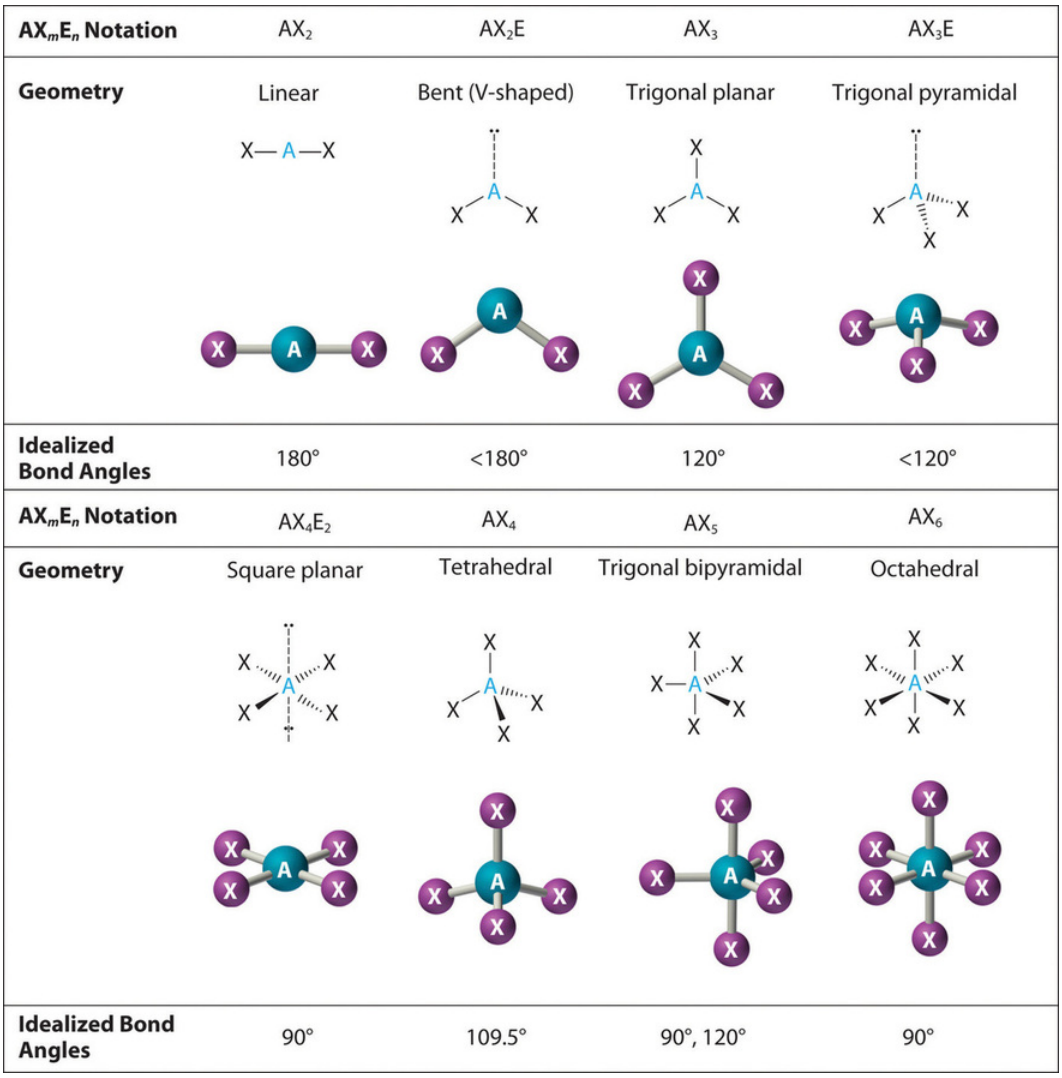


***Figure* 6.1.6.3:** *Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.*

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2 Molecules: 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 **6.1.6.2** that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure **6.1.6.3** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

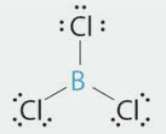
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure **6.1.6.3**). The structure of $\mathbf{CO_2}$ is shown in Figure **6.1.6.1**.

Three Electron Groups

AX_3 Molecules: 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

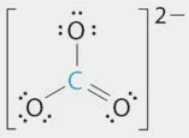
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure **6.1.6.2**).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure **6.1.6.3** we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure **6.1.6.2**.

AX_3 Molecules: 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

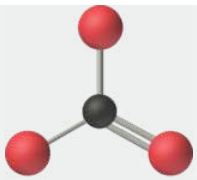


Lewis structure

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 **6.1.6.2**).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure **6.1.6.3** that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.

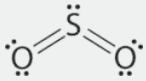


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E Molecules: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure **6.1.6.2**).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure **6.1.6.4**). 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 (Figures **6.1.6.2** and **6.1.6.3**). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

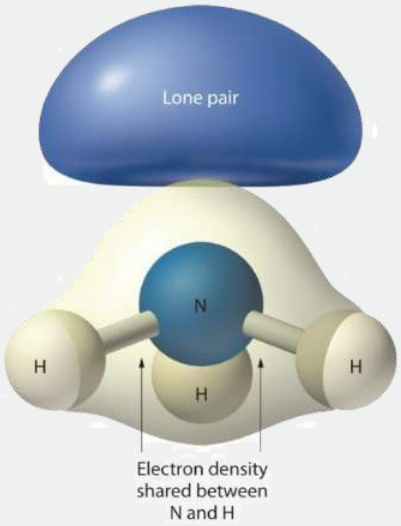
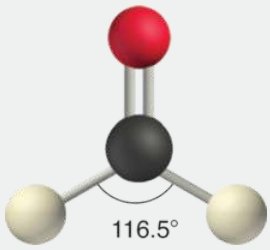


Figure* 6.1.6.4*: *The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair*

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°).

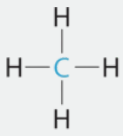


Four Electron Groups

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 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

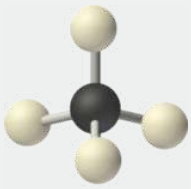


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure **6.1.6.2**, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

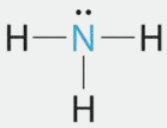
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure **6.1.6.3**).



Molecular geometry
(tetrahedral)

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

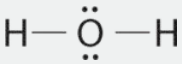
3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the

angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure **6.1.6.3**). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure **6.1.6.3** and Figure **6.1.6.4**).

AX_2E_2 Molecules: H_2O

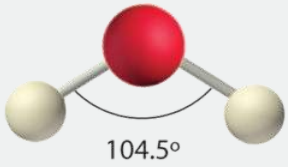
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure **6.1.6.2**.

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.

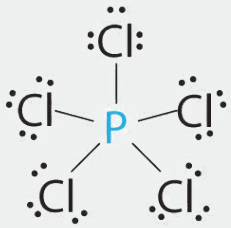


Five Electron Groups

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 Molecules: PCl_5

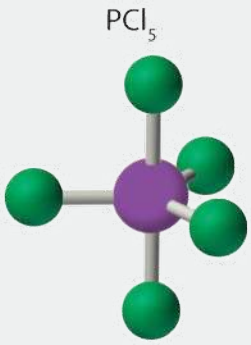
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



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 **6.1.6.2**):

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure **6.1.6.3**. 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 Molecules: 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 **6.1.6.2**.

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 axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

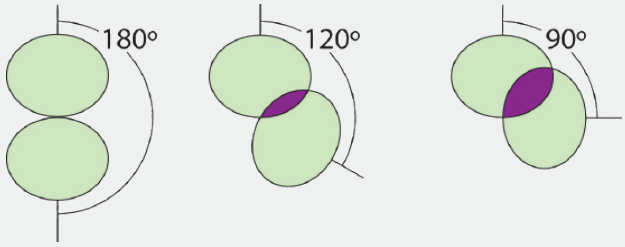
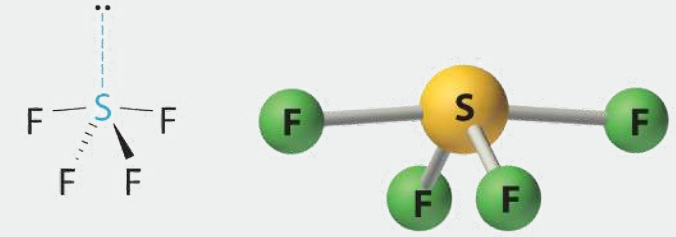


Figure* 6.1.6.5*: *Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them*

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

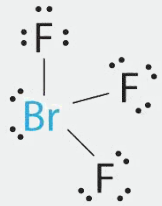
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: 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 **6.1.6.2**.1).

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.

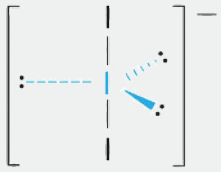
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



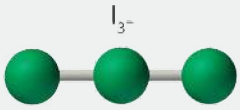
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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 **6.1.6.2.**)

AX_6 Molecules: 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



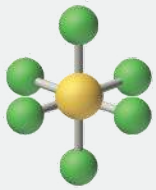
Lewis structure

With an expanded valence, 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 **6.1.6.2** 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.

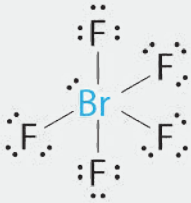
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E Molecules: BrF_5

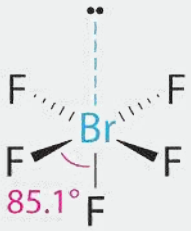
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

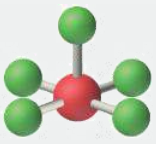
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

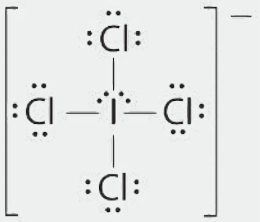
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



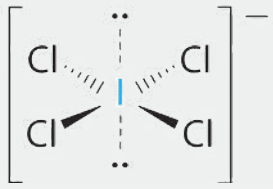
Molecular geometry
(square pyramidal)

AX_4E_2 Molecules: 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

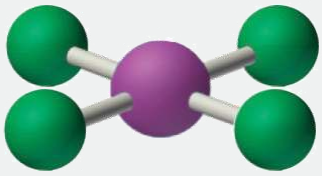


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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 **6.1.6.6**.

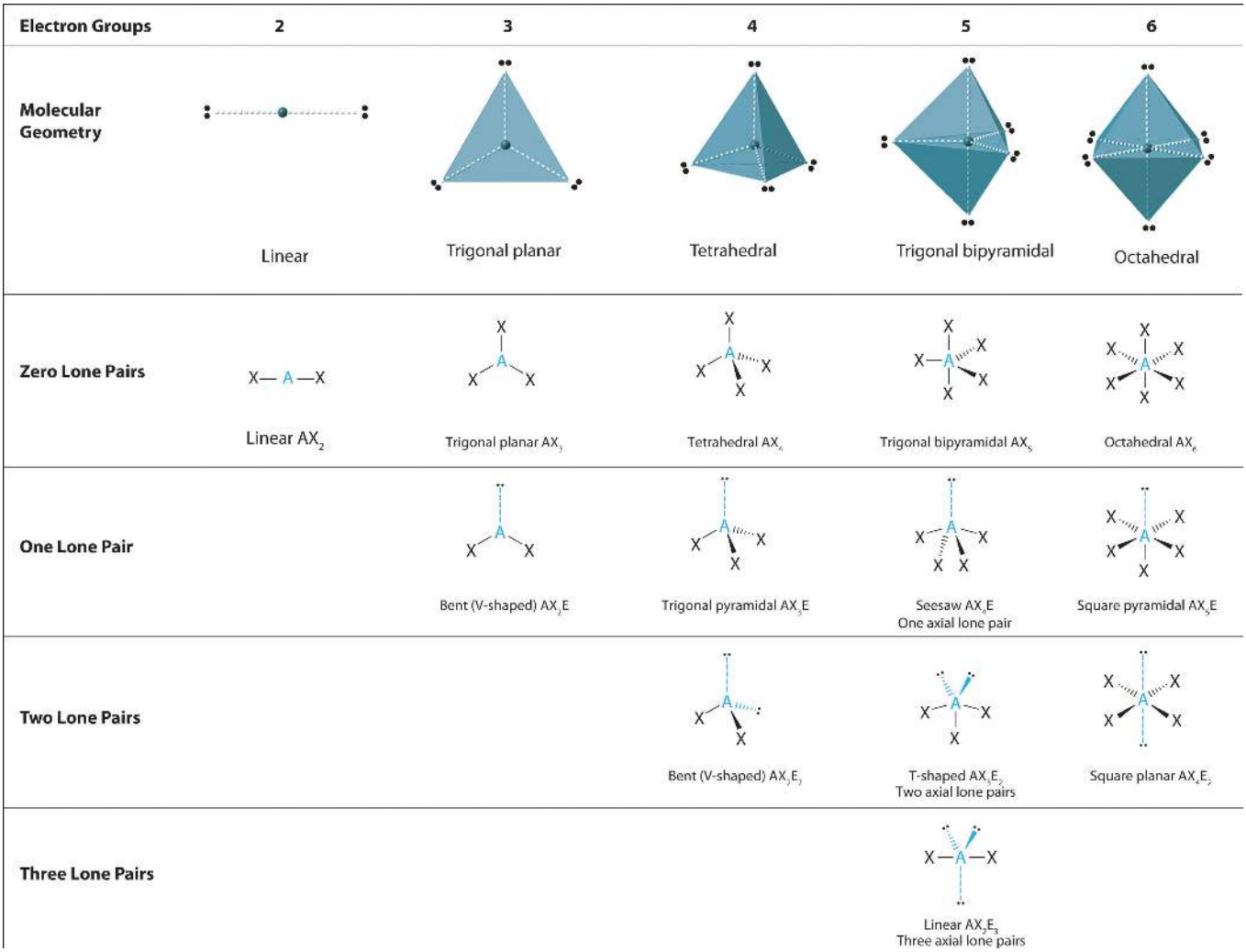


***Figure* 6.1.6.6:** *Overview of Molecular Geometries*

Example 6.1.6.1

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_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

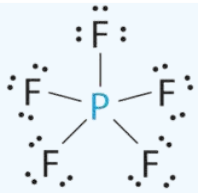
Strategy:

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

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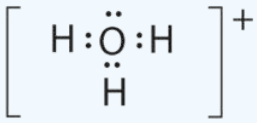
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure **6.1.6.6**).

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.



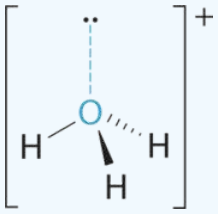
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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 6.1.6.1

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

Answer b

octahedral

Answer c

linear

Example 6.1.6.2

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**6.1.6.1**.

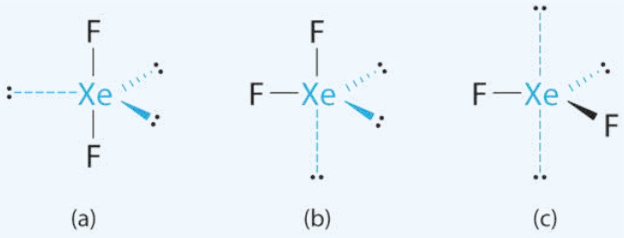
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:

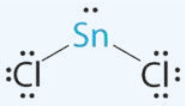


Interactions			
90 LP–LP	0	2	2

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise 6.1.6.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

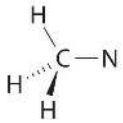
Answer b

square planar

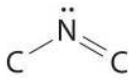
Molecules with No Single Central Atom

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:

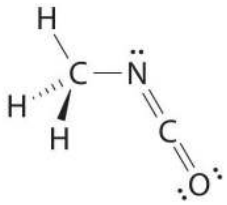


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



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 **6.1.6.7**).

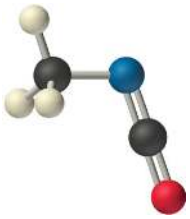


Figure* 6.1.6.7*: *The Experimentally Determined Structure of Methyl Isocyanate*

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 6.1.6.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C{\equiv}CH$), 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 **6.1.6.3** 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 6.1.6.3

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°.

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**. 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. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

6.1.6: The VSEPR Model is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

6.1.7: Molecular Polarity

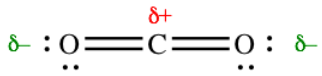
Learning Objectives

- To predict whether a molecule is polar or non-polar

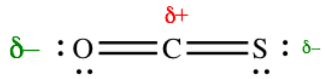
Introduction to Molecular Polarity

You have already seen that covalent bonds are polar when they link two different atoms. In a polar bond, one atom is positively charged and the other is negatively charged. A **molecule** (or polyatomic ion) is polar when one side of the molecule is more positive (or more negative) than the other. This occurs when the polarities of the bonds do not cancel out.

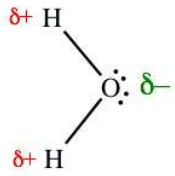
For example in CO_2, each carbon-oxygen bond is polar, but CO_2 is a **nonpolar molecule**. The molecule is linear, so the two bonds point in opposite directions. They are equally polar, so their effects cancel out. The two sides of the molecule are identical; neither one is more negative than the other.



On the other hand, OCS is a **polar molecule**. This molecule is also linear, but the C=O and C=S bonds are not equally polar, because O is more electronegative than S. In this molecule, the oxygen side is more negative than the sulfur side.



Water is also polar, but for a different reason. In this case, the two bonds are equally polar, but they do not cancel each other out, because they do not point in opposite directions. Water is a bent molecule, so the O–H bonds are roughly 109.5˚ apart (actually about 105˚). In the drawing below, the left side of the molecule is positively charged and the right side is negatively charged.



As a general rule, *molecules that are distorted are also polar*. The only exceptions are linear molecules in which the outer atoms are dissimilar; these molecules are not distorted, but they are polar. OCS (above) is an example.

Polar Molecules Have a Net Dipole Moment

Molecular polarity can be described more formerly in terms of the summation of bond **dipole moments**. In 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 (Figure **6.1.7.1*a***). 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 (Figure **6.1.7.1*b***); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

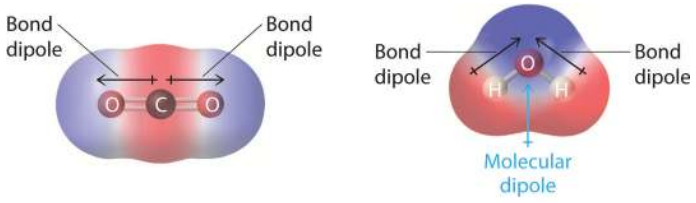


Figure **6.1.7.1**: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure **6.1.7.2**. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

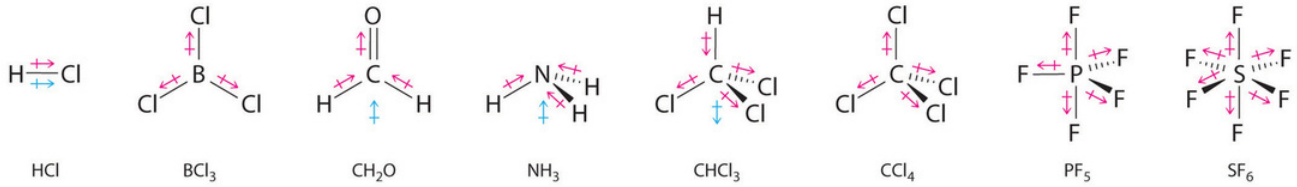


Figure **6.1.7.2**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

Molecules with asymmetrical charge distributions have a net dipole moment.

Example 6.1.7.1

Which molecule(s) has a net dipole moment?

a. **H_2S**
b. **NHF_2**
c. **BF_3**

Given: three chemical compounds

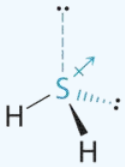
Asked for: net dipole moment

Strategy:

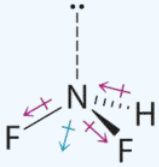
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

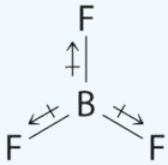
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of **H_2S** is bent (Figure **6.1.7.6**). The bond dipoles cannot cancel one another, so the molecule 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 6.1.7.1

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl and XeO_3

Summary

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.

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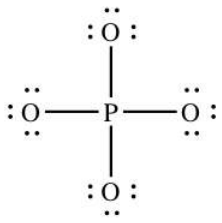
6.1.8: A Different Perspective on Drawing Lewis Structures

Learning Objectives

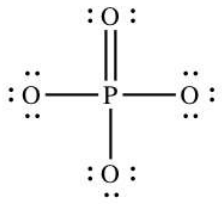
- Recognize that using formal charges to determine how many bonds to make, is different perspective on drawing Lewis Structures.

Using formal charges to determine how many bonds to make, a different perspective...

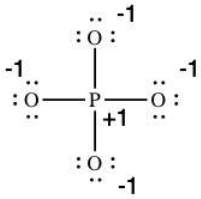
If we draw the Lewis structure for PO_4^{3-} ion using the rules you've seen earlier, we come up with the structure below. It has the correct number of electrons (32), and every atom satisfies the octet rule.

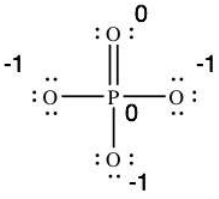


However, many textbooks (and websites) insist that the structure below is a better one, even though the phosphorus atom has ten electrons around it:



The first structure follows the rules for drawing structures. So why do chemists add a double bond? To understand, we need the formal charges on the atoms in each structure…





Many chemists prefer the second structure because it gives us a couple of zeroes. However, the phosphorus atom in the second structure violates the octet rule. So which structure is best?? The answer is that **either structure is legitimate**. Both structures give us all of the information we need about phosphate ion; they allow us to predict the shape of the molecule, the angles between the bonds, and whether the molecule is polar.

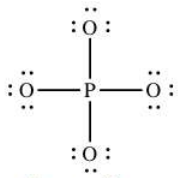
So which structure should YOU draw on a test? Be sure to check with your instructor, but most will accept either one. However, *the first structure is easier to figure out*, because it's the structure you produce when you follow the provided rules. The second structure requires more work. Therefore, we recommend that when you draw a structure that satisfies the octet rule, you stop there without adding more bonds.

WARNING: Some students come to Chem 101A having been taught to draw Lewis structures with extra double bonds.

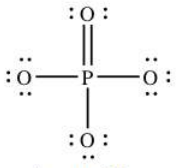
If you're familiar with Lewis structures and you like the extra bonds… congratulations! You have less to learn – you already know all of this stuff.

BUT…

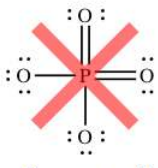
If you draw structures with extra bonds, they have to be correct. For example, a structure for phosphate that has two double bonds is not acceptable.



Acceptable

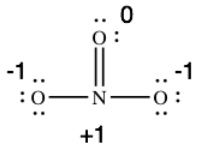


Acceptable



Not acceptable

Also, a structure for nitrate ion (NO_3^-) that has two double bonds is not acceptable, even though it gives you more zeroes. The structure with one double bond is the only acceptable one.



Acceptable



Not acceptable

If you don't know why the structures I've labeled "unacceptable" are not allowed, don't risk losing points by adding extra bonds when the central atom already has eight electrons.

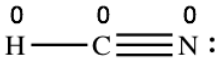
Using formal charges to evaluate which is the best central atom...

Generally, you are told which atom is the central bonding atom in the molecule. However, if it is unclear, or if you are asked to decide which atom is central, formal charges can be used to decide. The following is an example.

Example: calculating the formal charges in HCN and HNC

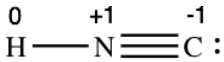
For the arrangement HCN, the Lewis structure: H–C≡N:

The formal charges work out as follows:



For the arrangement HNC, the Lewis structure: H–N≡C:

The formal charges work out as follows:



Both Lewis structures have a *net* formal charge of zero, but note that the formal charges on the first structure are all zero! Thus the first Lewis structure is predicted to be more stable, and it is, in fact, the structure observed experimentally. In general, the closer the formal charges are to zero, the more stable the structure. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a book-keeping method for predicting the most stable Lewis structure for a compound.

Summary

References

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CHAPTER OVERVIEW

6.2: Orbitals and Bonding Theories

6.2.1: Localized Electron Model of Covalent Bonding

6.2.2: Hybrid Atomic Orbitals

6.2.3: Orbital Overlap in Multiple Bonds

6.2.4: Molecular Orbital Theory

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6.2.1: Localized Electron Model of Covalent Bonding

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 $\mathbf{H_2O}$ and $\mathbf{NH_3}$, 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 $\mathbf{H_2O}$ and $\mathbf{NH_3}$. 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 $\mathbf{SrF_2}$ and $\mathbf{BaF_2}$, 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. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

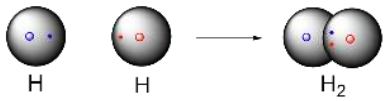
Introduction

As we have talked about using Lewis structures to depict the bonding in covalent 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?

The **valence bond theory** is introduced to describe bonding in covalent 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. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

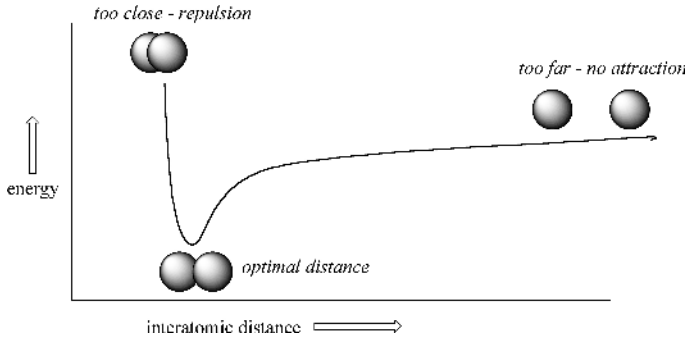
Example: The H_2 molecule

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. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



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. However, 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.



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.

Balls and Springs

Although we tend to talk about "bond length" as a specific distance, it is not accurate 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.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure **6.2.1.1**). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure **6.2.1.1**).

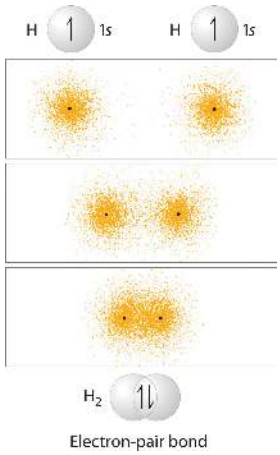


Figure **6.2.1.1**: *Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.*

Although Lewis 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 **6.2.1.2** 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 $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure **6.2.1.2**).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

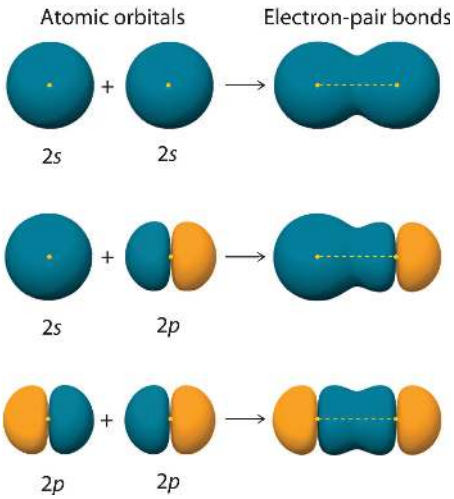
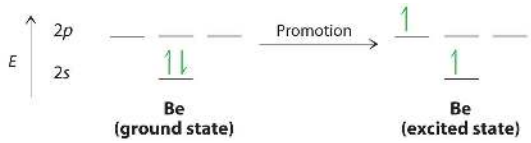


Figure **6.2.1.2** *: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.*

Let's examine the bonds in BeH_2, for example. 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 $\mathbf{BeH_2}$, 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 $\mathbf{BeH_2}$ form, scientists developed the concept of hybridization.

Contributors and Attributions

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6.2.2: Hybrid Atomic Orbitals

The localized **valence bond 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 **6.2.2.1**.

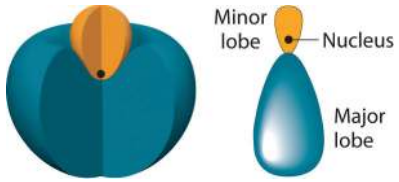


Figure 6.2.2.1: *The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.*

Because the difference A − B can also be written as A + (−B), in Figure **6.2.2.2** and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation **6.2.2.2**, 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.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{6.2.2.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{6.2.2.2}$$

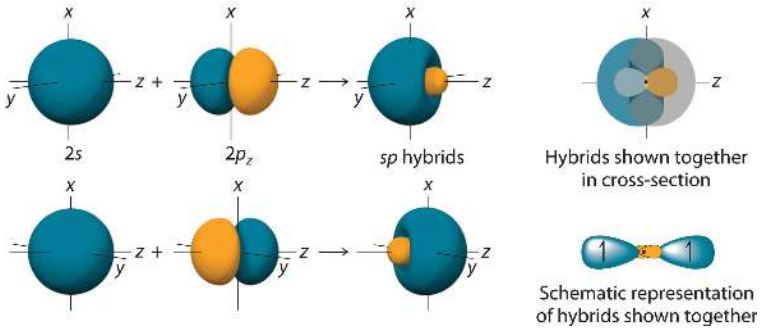
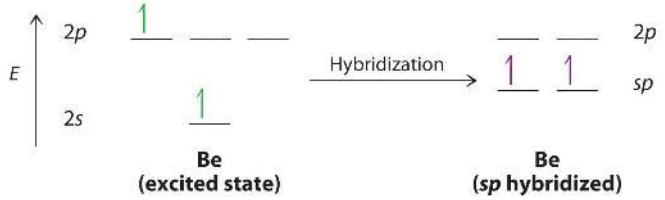


Figure **6.2.2.2**: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

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:



Each singly occupied *sp* hybrid orbital can now form an electron-pair bond with the singly occupied 1*s* atomic orbital of one of the H atoms. As shown in Figure **6.2.2.3**. 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 $\boldsymbol{BeH_2}$ 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 $\boldsymbol{BeH_2}$ are equivalent in energy and why $\boldsymbol{BeH_2}$ has a linear geometry.

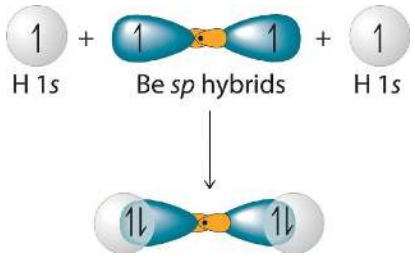


Figure **6.2.2.3**: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 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 **6.2.2.4**). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

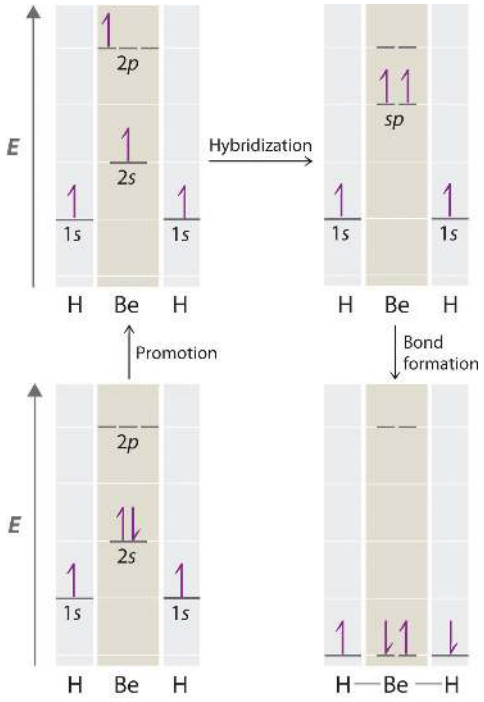
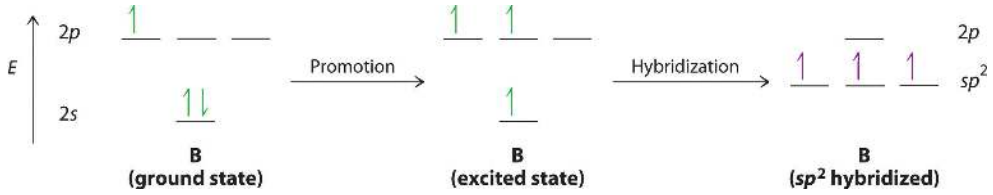


Figure **6.2.2.4**: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be 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.

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:



The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure **6.2.2.5**). 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.

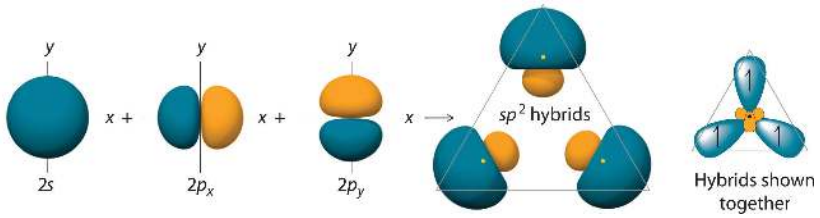
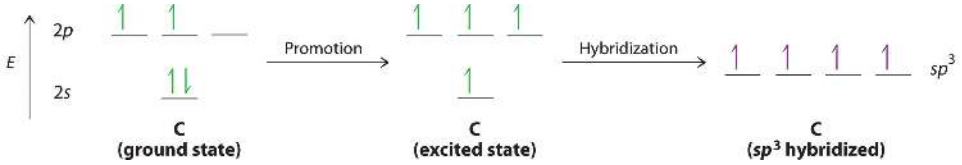


Figure **6.2.2.5**: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure **6.2.2.6**). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

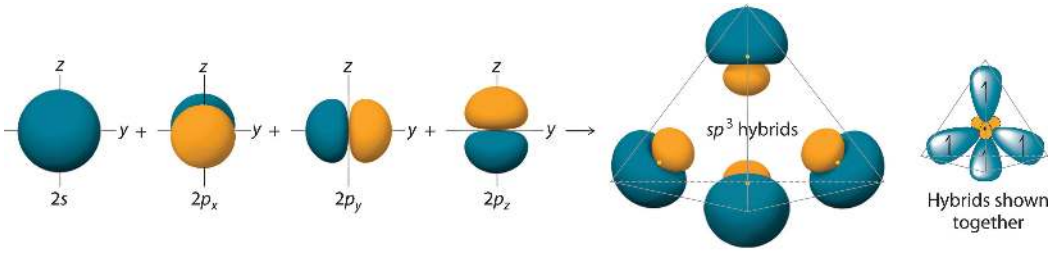


Figure **6.2.2.6**: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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 only form in 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 NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

Example 6.2.2.1

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 VSEPR 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 6.2.2.1

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.

Answer 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 **6.2.2.7**). 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 9.5.6). 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.

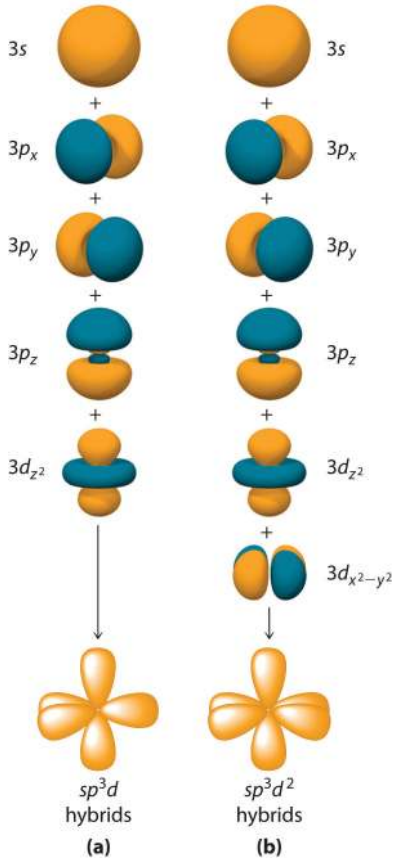


Figure **6.2.2.7**: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 6.2.2.2

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 **6.2.2.1**. 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 6.2.2.2

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

Answer a

sp^3d with three Br–F bonds and two lone pairs

Answer a

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 6.2.2.3: 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 6.2.2.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer a

sp^3d^2 hybridization; no

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 sp^2 **hybrids** or four equivalent 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 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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6.2.3: Orbital Overlap in Multiple Bonds

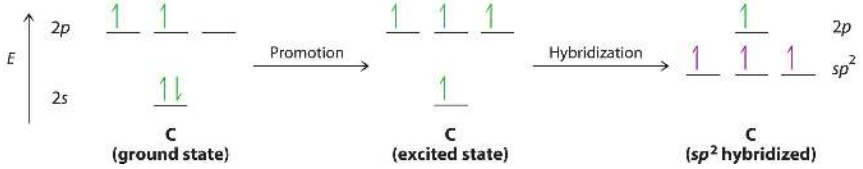
Learning Objectives

- To explain double and triple bonds in terms of orbital overlap

So far in our valence bond 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 unhybridized *np* atomic orbitals.

Multiple 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. The sp^2 hybridization can be represented as follows:



With this hybridization, each carbon forms a trigonal planar set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part (a) in Figure **6.2.3.1**). After hybridization, however, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure **6.2.3.1**). These two singly occupied $2p_z$ orbitals can overlap in a side-to-side fashion to form a π bond. The orbitals overlap both above and below the plane of the molecule but form just one bonding orbital space. The C–C π bond plus the hybridized C–C σ bond together form a double bond.

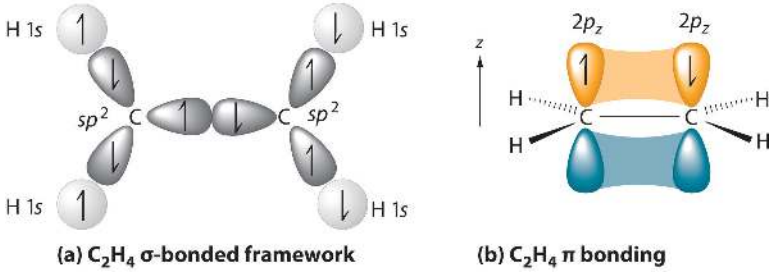
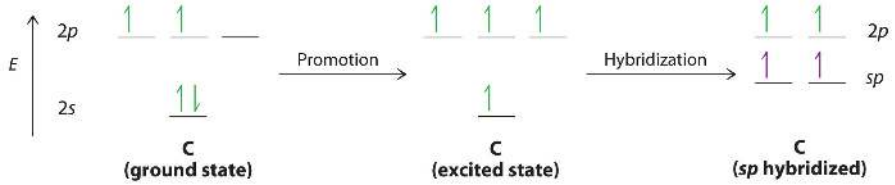


Figure **6.2.3.1**: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (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.)

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and unhybridized np orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure **6.2.3.3**).



The two 2*p* orbitals on each carbon can align with the corresponding 2*p* orbitals on the adjacent carbon to simultaneously form a *pair* of π bonds (part (b) in Figure **6.2.3.2**). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are

available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

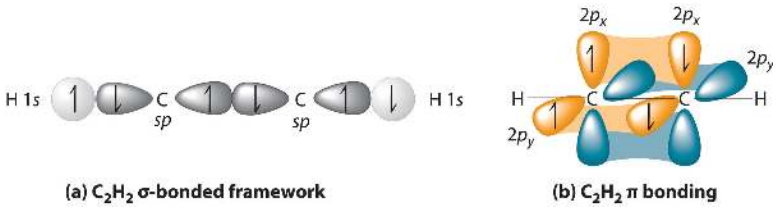


Figure **6.2.3.3**: Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon *sp* hybrid orbitals and two singly occupied hydrogen 1*s* orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

Example 6.2.3.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and unhybridized p orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and p orbitals

Strategy:

A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework.
B. Use any remaining unhybridized *p* orbitals to form π bonds.

Solution:

- σ-bonding framework: an unhybridized s orbital on hydrogen overlaps with an *sp* hybrid orbital on carbon, *sp* hybrid orbital on carbon overlaps with an *sp* hybrid orbital on nitrogen
- π bonding: unhybridized *p* atomic orbitals on carbon and nitrogen overlap to form a π bond.

Exercise 6.2.3.1

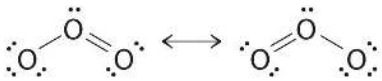
Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen overlap to form a π bond.

Orbital Overlap and Resonance Structures

Resonance structures can be used to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). Ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in Figure **6.2.3.4**. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.

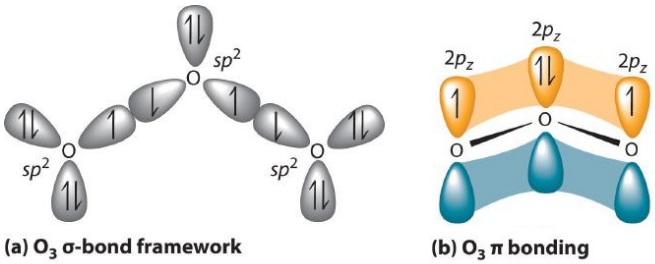


Figure **6.2.3.4**: Bonding in Ozone. (a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

Example 6.2.3.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and unhybridized p orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

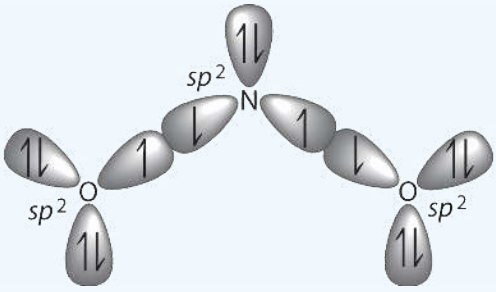
Strategy:

A. From the structure, predict the type of atomic orbital hybridization in the ion the central atom.
B. Use hybrid orbitals to form the σ-bonding framework.
C. Use hybrid orbitals to form the π bonding.

Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2*p* orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three 2*p* orbitals can overlap to form pi bonds.



Exercise 6.2.3.2

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer

Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized 2*p* orbitals (on C and both O atoms) overlap to form π bonds. The overall C–O bond order is therefore $frac32$

Summary

Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and unhybridized p orbitals to describe π bonding.

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6.2.4: 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.

6.2.4.1: 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*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom B) \\ MO(1) &= AO(atom\ A) - AO(atom B) \end{aligned} \tag{6.2.4.1}$$

The molecular orbitals created from Equation 6.2.4.1 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 **6.2.4.1**). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

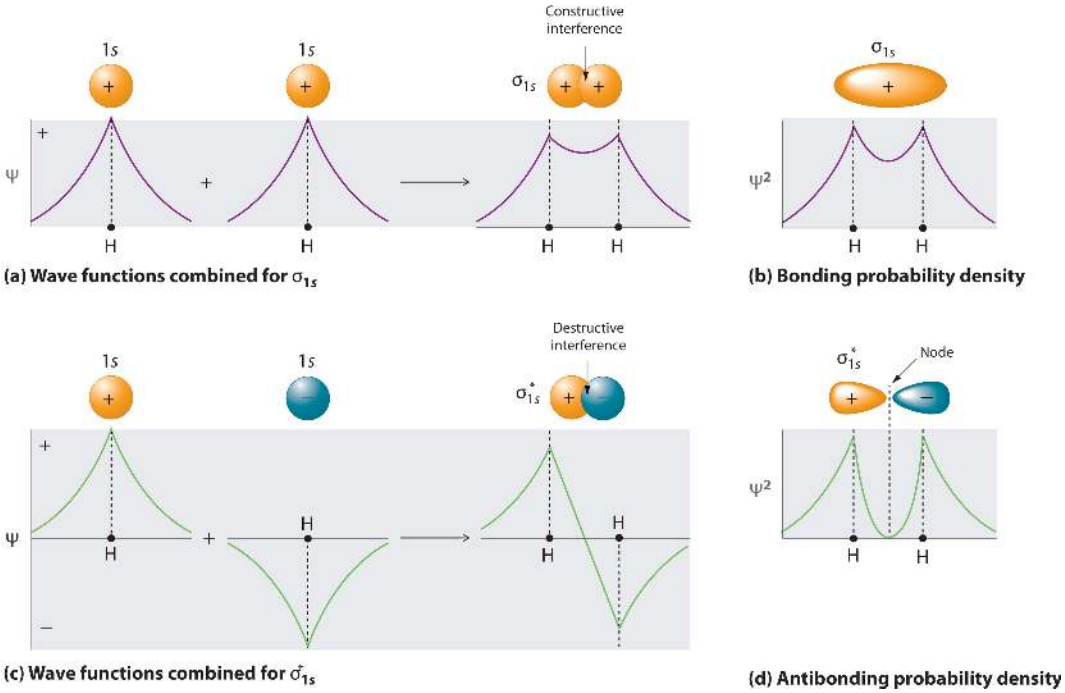


Figure **6.2.4.1**: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular 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.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{6.2.4.2}$$

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 **6.2.4.1**). 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:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{6.2.4.3}$$

> *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 σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{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.*

6.2.4.2: 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 σ^*_{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 σ^*_{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 σ^*_{1s} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure **6.2.4.2**

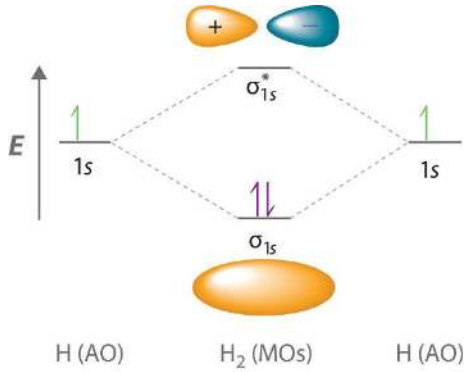


Figure **6.2.4.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is 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 **6.2.4.2**). 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.

6.2.4.3: 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:

$$\textit{bond order} = \frac{\textit{number of bonding electrons} - \textit{number of antibonding electrons}}{2} \tag{6.2.4.4}$$

To calculate the bond order of H_2, we see from Figure **6.2.4.2** that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{6.2.4.5}$$

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 **6.2.4.2** 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.

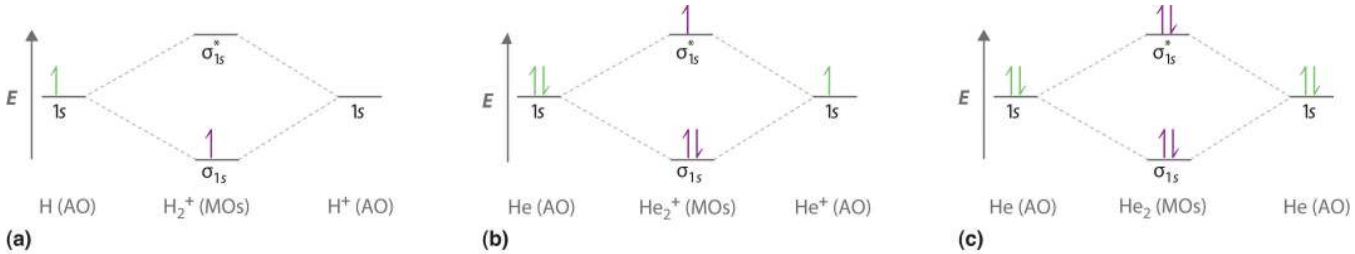


Figure **6.2.4.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure **6.2.4.3** 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 **6.2.4.1**, these predictions agree with the experimental data.

Part (b) in Figure **6.2.4.3** 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 σ^*_{1s} antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table **6.2.4.1**).

Table **6.2.4.1**: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure **6.2.4.3** is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ^*_{1s} antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.



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 6.2.4.1

Use a molecular orbital energy-level diagram, such as those in Figure **6.2.4.3**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

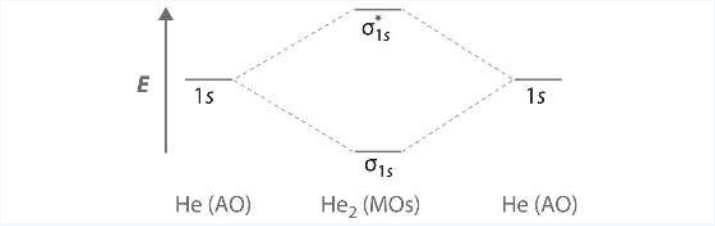
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

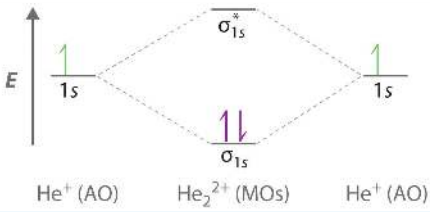
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning 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 6.2.4.1

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 $(\sigma_{1s})^2(\sigma^*_{1s})^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure **6.2.4.4**, 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 **6.2.4.2**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

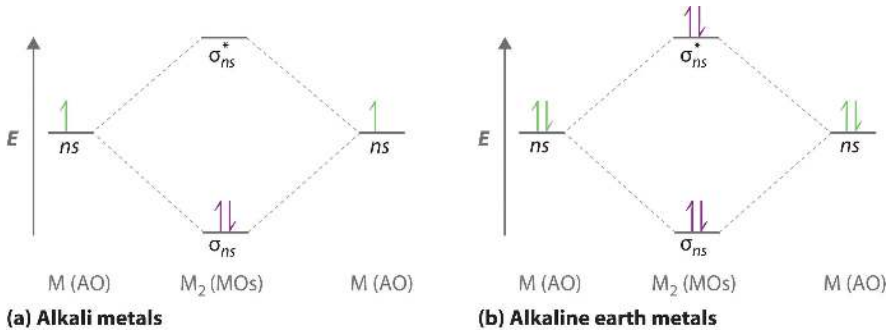


Figure **6.2.4.4**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 **6.2.4.3** As shown in part (b) in Figure **6.2.4.4**, 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, $\boldsymbol{Be_2}$ is stable.

Example 6.2.4.2

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

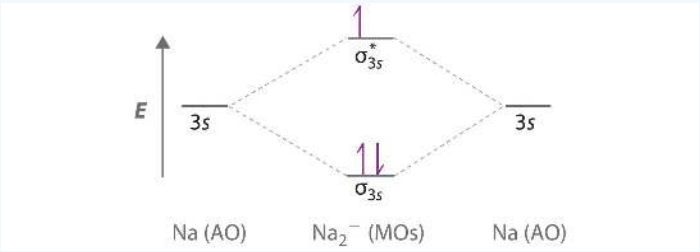
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

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 $(\sigma_{3s})^2(\sigma^*_{3s})^1$ 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 6.2.4.2

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 $(\sigma_{4s})^2(\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

6.2.4.4: 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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{6.2.4.6}$$

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 **6.2.4.5**, 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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{6.2.4.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{6.2.4.8}$$

In this combination, shown in part (b) in Figure **6.2.4.5**, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

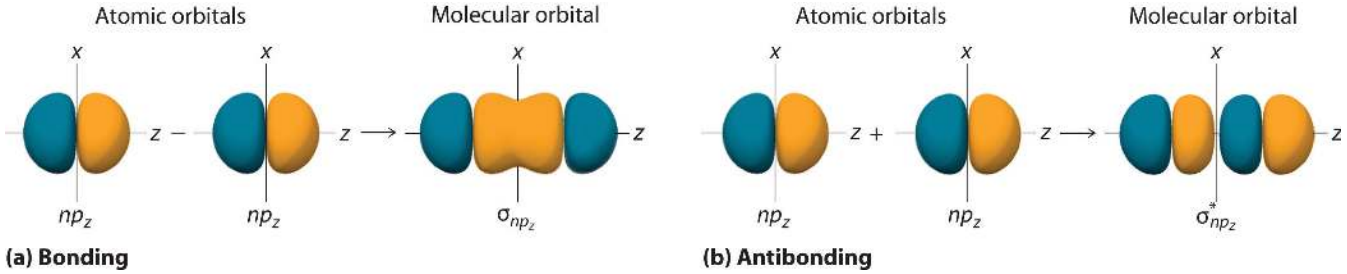


Figure **6.2.4.5**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two 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 **6.2.4.6**, 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..

$$\pi_{np_z} = np_x(A) + np_x(B) \tag{6.2.4.9}$$

$$\pi^*_{np_z} = np_x(A) - np_x(B) \tag{6.2.4.10}$$

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 $\pi^*_{np_y}$ 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_z} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

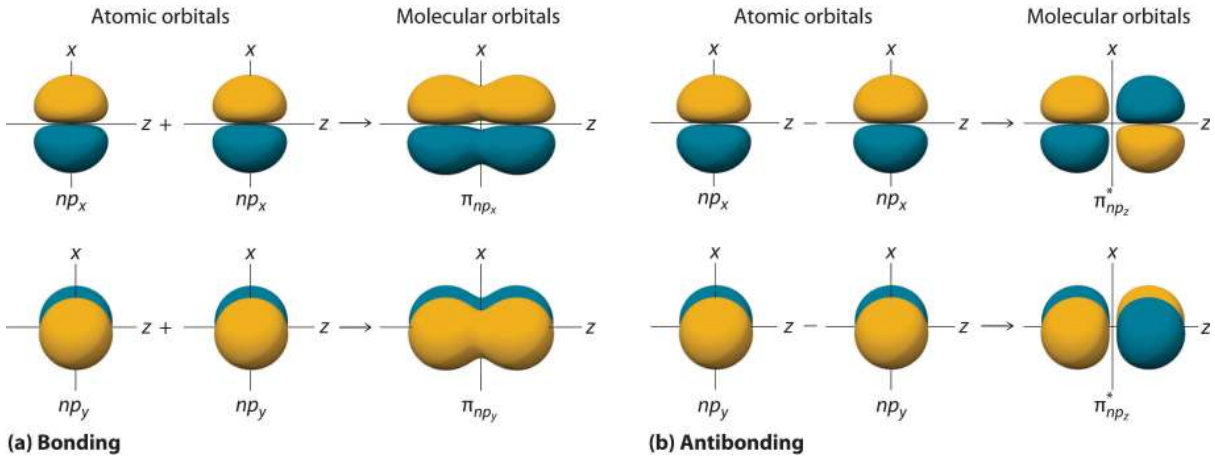


Figure 6.2.4.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 6.2.4.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

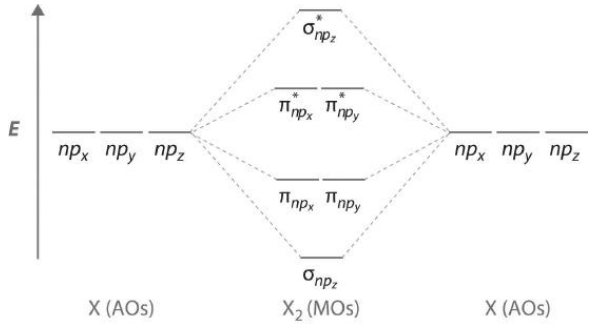


Figure 6.2.4.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 6.2.4.8, 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.

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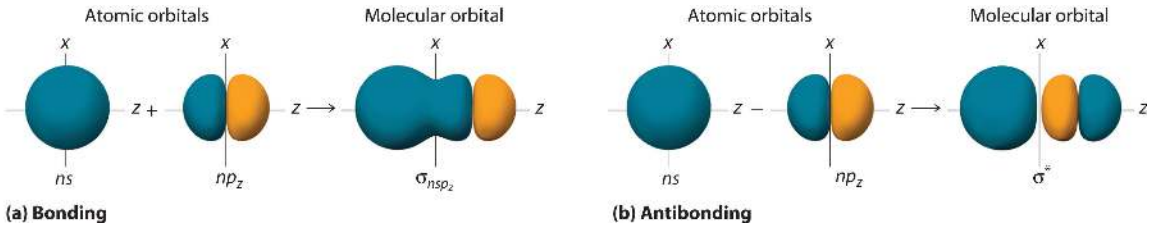


Figure **6.2.4.8**: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

6.2.4.5: 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 **6.2.4.9**; 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 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is 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 $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ 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.

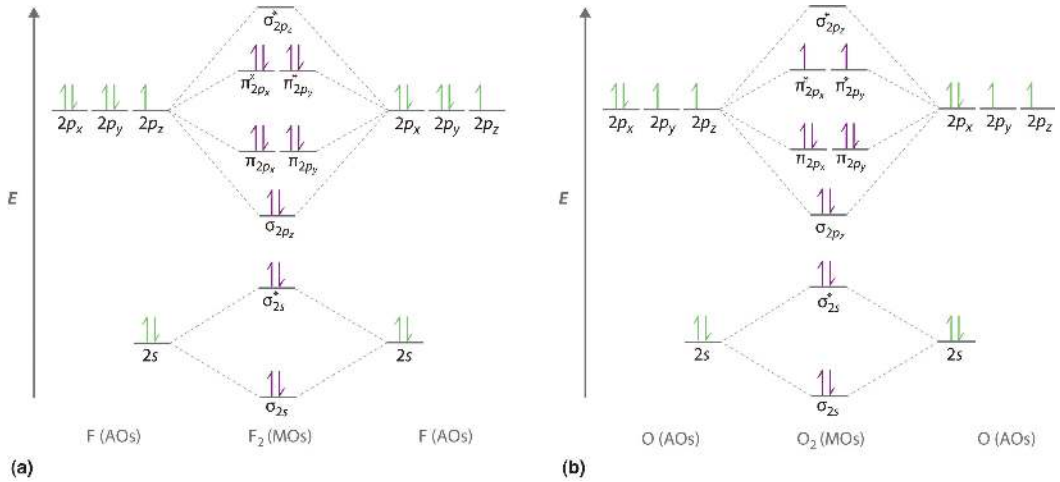


Figure **6.2.4.9**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ 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 **6.2.4.9**. 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 $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ 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 **6.2.4.10**, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



Figure **6.2.4.10**: 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 $\pi^*_{np_x}$ and $\pi^*_{np_y}$ 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 **6.2.4.11** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **6.2.4.11**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

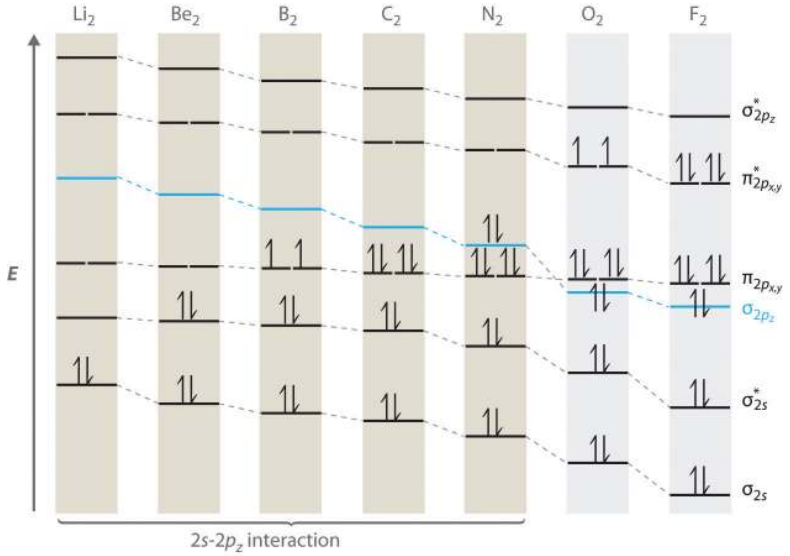


Figure **6.2.4.11**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. 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 6.2.4.3

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

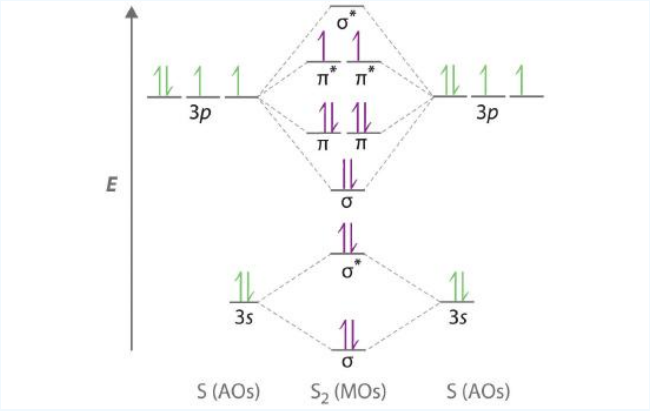
Strategy:

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]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure **6.2.4.9** and Figure **6.2.4.11**, 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 $\pi_{3p_{z,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **6.2.4.11**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{z,y}}$ 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 $\pi^*_{3p_x}$ and $\pi^*_{3p_y}$ 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 $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{z,y}})^4(\pi_{3p^*_{z,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 6.2.4.3

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

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{z,y}})^4(\pi_{2p^*_{z,y}})^4$

bond order of 1;

no unpaired electrons

6.2.4.6: 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 **6.2.4.12**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B.

Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

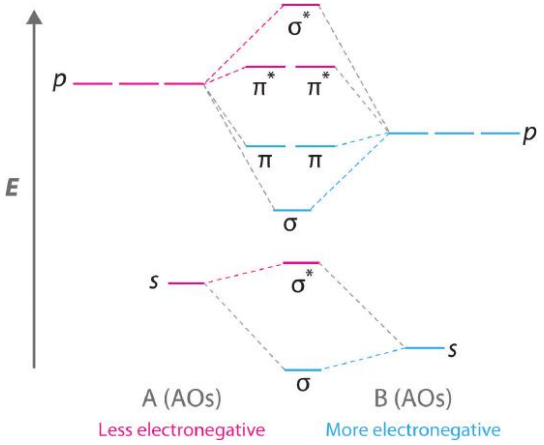


Figure **6.2.4.12**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared 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 **6.2.4.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure **6.2.4.11**). 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.

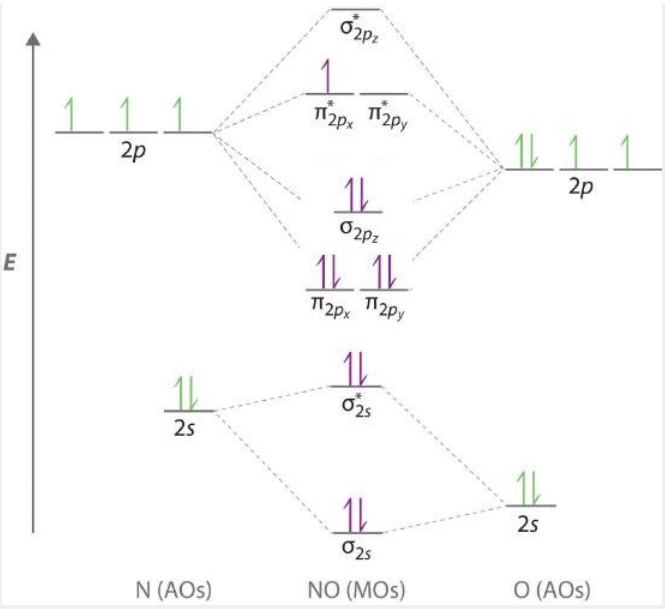


Figure **6.2.4.13**: Molecular Orbital Energy-Level Diagram for **NO**. Because **NO** has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^*_{2p_x}, \pi^*_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of **NO** to be $(\sigma_{2s})^2 (\sigma^*_{2s})^2 \left(\pi_{2p_{x,y}}\right)^4 (\sigma_{2p_z})^2 \left(\pi_{2p^*_{x,y}}\right)^2$ 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 **6.2.4.11**).

Molecular orbital theory can also tell us something about the *chemistry* of ***NO***. As indicated in the energy-level diagram in Figure **6.2.4.13**, 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

6.2.4.7: Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure **6.2.4.14** 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 $H^{\delta+}-Cl^{\delta-}$.

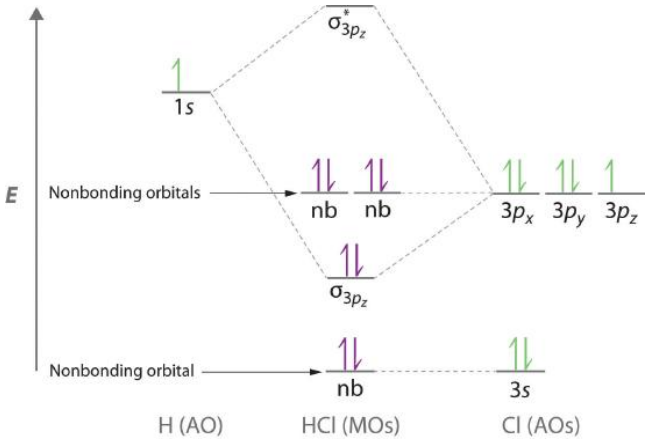


Figure **6.2.4.14**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have **no effect** on bond order.*

Example 6.2.4.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **6.2.4.12** to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

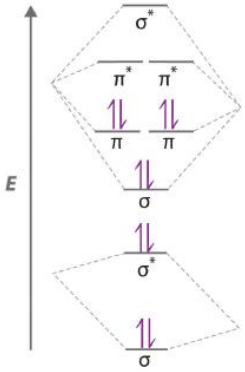
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **6.2.4.12** in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure **6.2.4.12** fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise 6.2.4.4

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.

6.2.4.8: 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.

6.2.4.9: Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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SECTION OVERVIEW

Topic G- Chemical Equilibrium

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

1. Write the equilibrium constant expression for a chemical reaction in terms of either partial pressures or molarities, and interconvert K_p and K for a gas-phase reaction.
2. Interpret the magnitude of an equilibrium constant.
3. Evaluate a reaction quotient, and use it to determine the direction of a reaction.
4. Calculate a value for the equilibrium constant, given appropriate concentrations or gas pressures, and use this value to determine concentrations/pressures in other equilibrium mixtures.
5. Calculate final concentrations/pressures of reactants and products, given appropriate information about the initial conditions.
6. Understand and apply le Châtelier's Principle.
7. Use the ion product of water (K_w) to relate the concentrations of H^+ and OH^- in an aqueous solution.
8. Write the K_a expression for an acid, and interpret the numerical value of K_a.
9. Calculate the pH of a solution of a strong acid or base, calculate the pH of a solution of a weak acid given its K_a value, and calculate the K_a of a weak acid given the pH of a solution of known molarity.
10. Identify the conjugate acid or base of a given species, and relate the strength of an acid to that of its conjugate base.

7.1: Chemical Equilibrium

7.1.1: The Concept of Equilibrium
7.1.2: The Equilibrium Constant
7.1.3: Heterogeneous Equilibria
7.1.4: Equilibrium Stoichiometry Calculations
7.1.5: Applications of Equilibrium Constants
7.1.6: Le Chatelier's Principle

7.2: Introduction to Acid–Base Equilibria

7.2.1: Brønsted–Lowry Acids and Bases
7.2.2: Autoionization of Water
7.2.3: pH and pOH
7.2.4: Acid Strength

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CHAPTER OVERVIEW

7.1: Chemical Equilibrium

In this chapter, we describe the methods chemists use to quantitatively describe the composition of chemical systems at equilibrium, and we discuss how factors such as temperature and pressure influence the equilibrium composition. As you study these concepts, you will also learn how urban smog forms and how reaction conditions can be altered to produce H_2 rather than the combustion products CO_2 and H_2O from the methane in natural gas. You will discover how to control the composition of the gases emitted in automobile exhaust and how synthetic polymers such as the polyacrylonitrile used in sweaters and carpets are produced on an industrial scale.

7.1.1: The Concept of Equilibrium
7.1.2: The Equilibrium Constant
7.1.3: Heterogeneous Equilibria
7.1.4: Equilibrium Stoichiometry Calculations
7.1.5: Applications of Equilibrium Constants
7.1.6: Le Chatelier's Principle

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7.1.1: The Concept of Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

For most of the reactions that we have discussed so far in general chemistry, you have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure 7.1.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. Figure used with permission from Wikipedia (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($\mathbf{N_2O_4}$) to nitrogen dioxide ($\mathbf{NO_2}$). You may recall that $\mathbf{NO_2}$ is responsible for the brown color we associate with smog. When a sealed tube containing solid $\mathbf{N_2O_4}$ (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of $\mathbf{NO_2}$ appears (Figure 7.1.1.1). The reaction can be followed visually because the product ($\mathbf{NO_2}$) is colored, whereas the reactant ($\mathbf{N_2O_4}$) is colorless:

$$\underset{\textit{colorless}}{\mathrm{N_2O_4(g)}} \rightleftharpoons \underset{\textit{red–brown}}{\mathrm{2\,NO_2(g)}} \tag{7.1.1.1}$$

The double arrow indicates that both the forward reaction

$$\mathrm{N_2O_4(g) \longrightarrow 2\,NO_2(g)} \tag{7.1.1.2}$$

and reverse reaction

$$\mathrm{2\,NO_2(g) \longrightarrow N_2O_4(g)} \tag{7.1.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is at equilibrium as the following chapter demonstrates.

Figure 7.1.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of $\mathbf{NO_2}$ were zero, then it increases as the concentration of $\mathbf{N_2O_4}$ decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no $\mathbf{N_2O_4}$ but an initial $\mathbf{NO_2}$ concentration twice the initial concentration of $\mathbf{N_2O_4}$ (Figure 7.1.1.2*a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 7.1.1.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

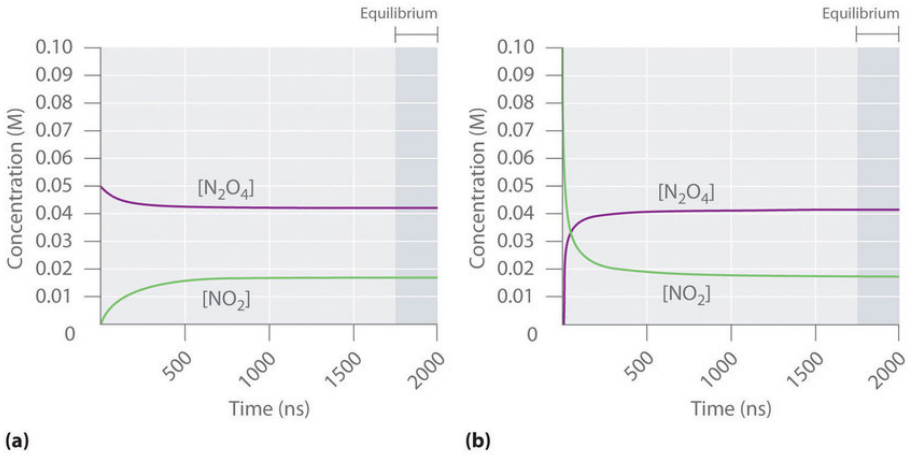


Figure 7.1.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium.

Figure 7.1.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 7.1.1.1 and ???). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

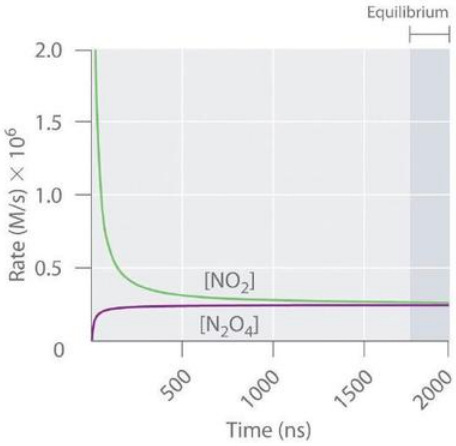


Figure 7.1.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_{2}O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ *System Shown in Part (b) in Figure* 7.1.1.2

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

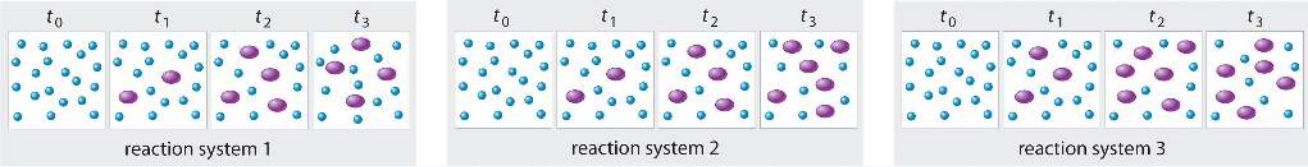
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 7.1.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B \tag{7.1.1.4}$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

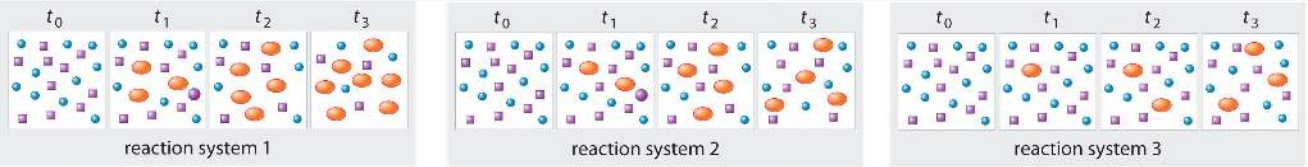
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 7.1.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer

system 2

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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7.1.2: The Equilibrium Constant

Learning Objectives

- To write an equilibrium constant expression for any homogenous reaction.
- To manipulate the equilibrium constant expression for various forms of an equation.
- To calculate an equilibrium constant from a sum of reactions with known K values.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction. In a future course, you will explore rates of reaction quantitatively. In this section, we will focus on the empirically observed changes in composition of the system.

Table **7.1.2.1** lists the initial and equilibrium concentrations from five different experiments using the reaction system described by:

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4$$

At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table **7.1.2.1**: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{7.1.2.1}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action (or law of chemical equilibrium) and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{7.1.2.2}$$

where K is the equilibrium constant for the reaction. Equation 7.1.2.1 is called the equilibrium equation, and the right side of Equation 7.1.2.2 is called the equilibrium constant expression. The relationship shown in Equation 7.1.2.2 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 7.1.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 7.1.2.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s)+O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2H_2(g)+O_2(g) \rightleftharpoons 2H_2O(g)$	500	2.4×10^{47}
$H_2(g)+Cl_2(g) \rightleftharpoons 2HCl(g)$	300	1.6×10^{33}
$H_2(g)+Br_2(g) \rightleftharpoons 2HBr(g)$	300	4.1×10^{18}
$2NO(g)+O_2(g) \rightleftharpoons 2NO_2(g)$	300	4.2×10^{13}
$3H_2(g)+N_2(g) \rightleftharpoons 2NH_3(g)$	300	2.7×10^{8}
$H_2(g)+D_2(g) \rightleftharpoons 2HD(g)$	100	1.92
$H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2I(g)$	800	$4.6 \times^{10-7}$
$Br_2(g) \rightleftharpoons 2Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 7.1.2.2 that equilibrium constants have no units, even though Equation 7.1.2.2 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 7.1.2.3, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{7.1.2.3}$$

> *Because equilibrium constants are calculated using "effective concentrations" relative to a standard state of 1 M, values of K are unitless.*

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_2(g) + D_2(g) \rightleftharpoons 2HD(g) \tag{7.1.2.4}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{7.1.2.5}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 7.1.2.3 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products. When K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when K is a very **small** number, and the reaction produces almost no products as written. Systems for which $K \approx 1$ have significant concentrations of both reactants and products at equilibrium.

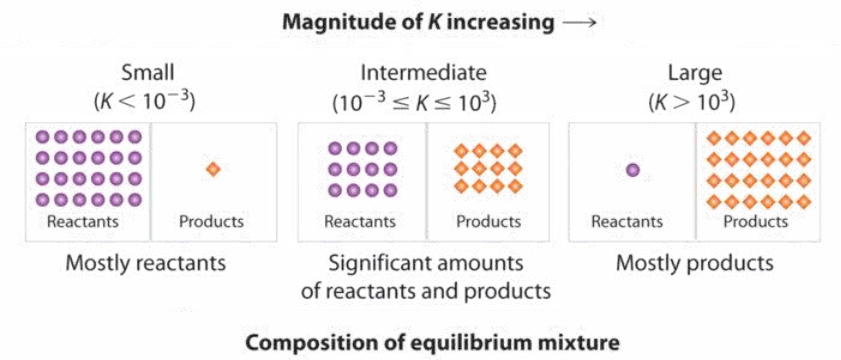


Figure 7.1.2.3: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

Example 7.1.2.1: equilibrium constant expressions

Write the for each reaction.

- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$
- $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 7.1.2.2. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{7.1.2.6}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{7.1.2.7}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{7.1.2.8}$$

Exercise 7.1.2.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O\,(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2\,(g)}$
b. $\mathrm{2\,C_8H_{18}\,(g) + 25\,O_2\,(g) \rightleftharpoons 16\,CO_2\,(g) + 18\,H_2O\,(g)}$
c. $\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 7.1.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $\mathrm{H_2(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \qquad K_{(700K)} = 54$
2. $\mathrm{2\,CO_2\,(g) \rightleftharpoons 2\,CO(g) + O_2\,(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $\mathrm{PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)} \qquad K_{(613K)} = 97$
4. $\mathrm{2\,O_3\,(g) \rightleftharpoons 3\,O_2\,(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 7.1.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3\,H_2\,(g) + N_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \tag{7.1.2.9}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 7.1.2.1 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{7.1.2.10}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{7.1.2.11}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{7.1.2.12}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{7.1.2.13}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> *The equilibrium constant for a reaction written in reverse is the inverse of the equilibrium constant for the reaction as written originally.*

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{7.1.2.14}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{7.1.2.15}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{7.1.2.16}$$

The values for K′ (Equation 7.1.2.13) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{7.1.2.17}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

Example 7.1.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{7.1.2.18}$$

What is the equilibrium constant for each related reaction at 745 K?

a. $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$
b. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118 \tag{7.1.2.19}$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47 \tag{7.1.2.20}$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344 \tag{7.1.2.21}$$

Exercise

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$$

Answer

3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{7.1.2.22}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{7.1.2.23}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The "effective pressure" is called the fugacity, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{7.1.2.24}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of **gaseous** products and **gaseous** reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 7.1.2.24, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \tag{7.1.2.25}$$

Example 7.1.2.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{7.1.2.26}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 7.1.2.24 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 7.1.2.17, we have the following:

$$\begin{aligned} K_p &= K(RT)^{-2} \\ &= \frac{K}{(RT)^2} \\ &= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} \\ &= 3.16 \times 10^{-5} \end{aligned}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 7.1.2.4

Calculate K_p for the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$

Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (step 1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$$

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^9$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{7.1.2.27}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{7.1.2.28}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^9) = 1.3 \times 10^{-15} \tag{7.1.2.29}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

> *To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.*

Example 7.1.2.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{7.1.2.30}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{7.1.2.31}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{7.1.2.32}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3} \tag{7.1.2.33}$$

Exercise 7.1.2.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Summary

For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. Under a given set of conditions, a reaction will always have the same K. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p)

is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{7.1.2.34}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{7.1.2.35}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n} \tag{7.1.2.36}$$

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7.1.3: Heterogeneous Equilibria

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)} \tag{7.1.3.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2} a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{7.1.3.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{7.1.3.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and $\mathrm{CO_2}$, the system described in Equation 7.1.3.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure **7.1.3.1**, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

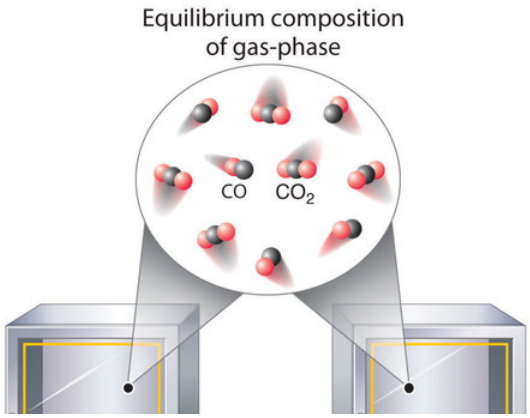
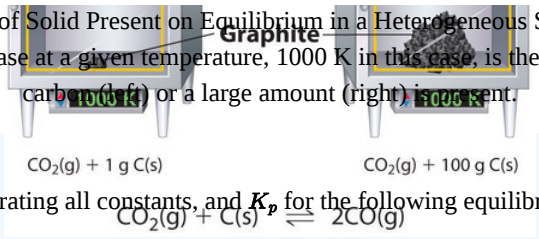


Figure 7.1.3.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.



Example 7.1.3.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)}$
b. $\mathrm{Fe_3O_4(s) + 4\,H_2(g) \rightleftharpoons 3\,Fe(s) + 4\,H_2O(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

Exercise 7.1.3.1

Write the expressions for K and K_p for the following reactions.

a. $\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$
b. $\underset{\textit{glucose}}{\mathrm{C_6H_{12}O_6(s)}} + \mathrm{6\,O_2(g) \rightleftharpoons 6\,CO_2(g) + 6\,H_2O(g)}$

Answer a

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

Answer b

$$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6} \text{ and } K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium

constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

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7.1.4: Equilibrium Stoichiometry Calculations

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

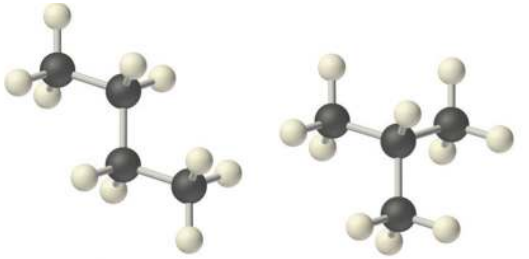
There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

The equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.1.4.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{7.1.4.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 7.1.4.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n} \tag{7.1.4.3}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

Exercise 7.1.4.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer

$K = 48.8$ and $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example **7.1.4.2** shows one way to do this.

Example 7.1.4.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise 7.1.4.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 7.1.4.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 7.1.4.2.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.1.4.4}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.1.4.5}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00-x)$	$(0+x)=x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K=\frac{[\text{isobutane}]}{[\text{n-butane}]}=\frac{x}{1.00-x}=2.6 \tag{7.1.4.6}$$

Rearranging and solving for x,

$$x=2.6(1.00-x)=2.6-2.6x \tag{7.1.4.7}$$

$$x+2.6x=2.6 \tag{7.1.4.8}$$

$$x=0.72 \tag{7.1.4.9}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f=(1.00-x)M=(1.00-0.72)M=0.28\ M \tag{7.1.4.10}$$

$$[\text{isobutane}]_f=(0.00+x)M=(0.00+0.72)M=0.72\ M \tag{7.1.4.11}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K=\frac{[\text{isobutane}]}{[\text{n-butane}]}=\left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right)=2.6 \tag{7.1.4.12}$$

This is the same K we were given, so we can be confident of our results.

Example **7.1.4.3** illustrates a common type of equilibrium problem that you are likely to encounter.

Example 7.1.4.3: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.0150 - x)$	$(0.0150 - x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150 - x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$

- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise 7.1.4.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f = 0.270\ M$
- $[H_2]_f = [I_2]_f = 0.037\ M$

In Example **7.1.4.3**, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example **7.1.4.4**.

Example 7.1.4.4

In the water–gas shift reaction shown in Example **7.1.4.3**, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570-x)$	$(0.632-x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{x^2}{(0.570-x)(0.632-x)}=0.106$$

In contrast to Example **7.1.4.3**, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2=0.106(0.360-1.202x+x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2+0.127x-0.0382=0$$

This equation can be solved using the quadratic formula:

$$x=\frac{-b\pm\sqrt{b^2-4ac}}{2a}=\frac{-0.127\pm\sqrt{(0.127)^2-4(0.894)(-0.0382)}}{2(0.894)}$$

$$x=0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O]=\Delta[CO]=+0.148M$, and $\Delta[H_2]=\Delta[CO_2]=-0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[=[H_2]_i+\Delta[H_2]=0.570\ M-0.148\ M=0.422M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=0.632\ M-0.148\ M=0.484M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=0\ M+0.148\ M=0.148\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=0M+0.148\ M=0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.148)^2}{(0.422)(0.484)}=0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise 7.1.4.4

The exercise in Example **7.1.4.1** showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K=54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

- $[H_I]_f=0.0882\ M$
- $[H_2]_f=0.156\ M$
- $[I_2]_f=9.2\times10^{-4}M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K\leq10^{-3}$) or very large ($K\geq10^3$), which means that the change in the

concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example **7.1.4.5**.

Example 7.1.4.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2} = 0.78\ atm$ and $P_{O_2} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$
Final	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) = 0.78$ and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise 7.1.4.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^{3}$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 7.1.4.6.

Example 7.1.4.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).

C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example **7.1.4.5**. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	$+x$	$+x$	$-x$
Final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x)$ = 0.045 and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

Exercise 7.1.4.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M\ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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7.1.5: Applications of Equilibrium Constants

Learning Objectives

- To predict in which direction a reaction will proceed.

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a Quantity called the reaction Quotient (Q). The expression for the reaction Quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightleftharpoons cC + dD \tag{7.1.5.1}$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{7.1.5.2}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{7.1.5.3}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{7.1.5.4}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = \frac{[NO^2]^2}{[N^2O^4]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is

greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 7.1.5.1.

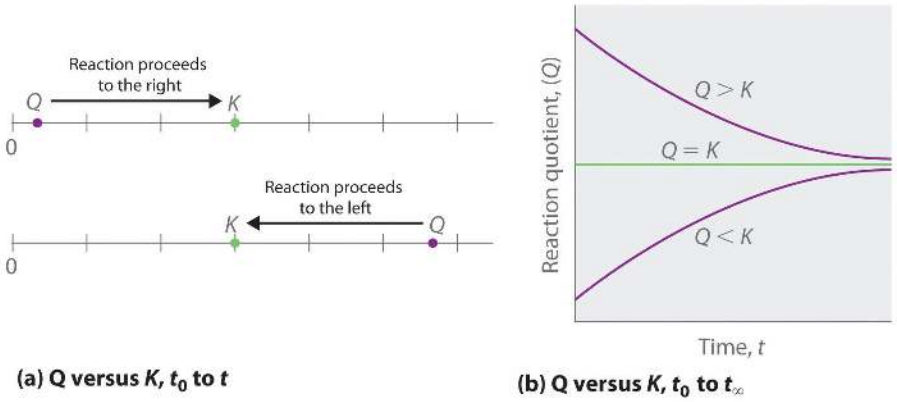


Figure 7.1.5.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

> *If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.*

Example 7.1.5.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \tag{7.1.5.5}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 7.1.5.2 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M \tag{7.1.5.6}$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B We now compute Q and compare it with K:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6} \tag{7.1.5.7}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

Exercise 7.1.5.2

In the water–gas shift reaction introduced in Example 7.1.5.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \tag{7.1.5.8}$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$. Since (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_{3(s)} \rightleftharpoons PbO_{(s)} + CO_{2(g)} \tag{7.1.5.9}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 7.1.5.3, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only CO2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 7.1.5.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (Q > K). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 7.1.5.9 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 7.1.5.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (Q < K). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 7.1.5.9 will therefore proceed to the right as written, until $[CO_2] = K$.

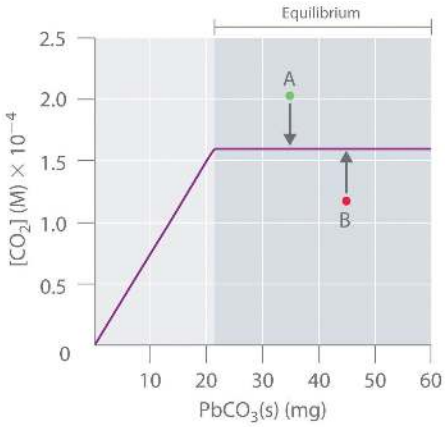


Figure **7.1.5.2**: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)} \tag{7.1.5.10}$$

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure **7.1.5.3**). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 7.1.5.10 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure **7.1.5.3**lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (Q < K). Thus the reaction in Equation 7.1.5.10 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure **7.1.5.3** lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture (Q > K). Thus the reaction in Equation 7.1.5.10 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

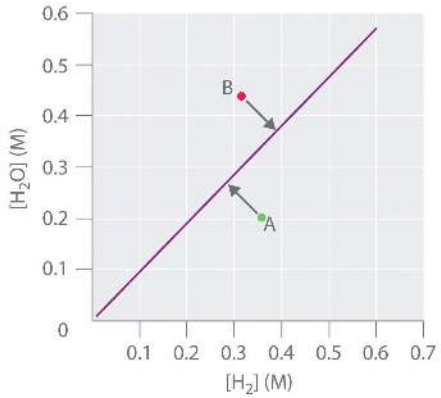


Figure **7.1.5.3**: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{7.1.5.11}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure **7.1.5.4**. As

a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure **7.1.5.4**) corresponds to $Q < K$, and the reaction in Equation 7.1.5.11 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 7.1.5.11) corresponds to $Q > K$, and the reaction in Equation 7.1.5.11 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

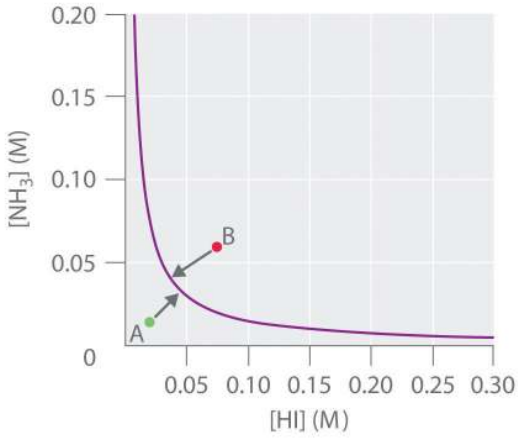


Figure **7.1.5.4**: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Summary

The reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. The reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

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7.1.6: Le Chatelier's Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if ($Q \leq K$) or the reactants (if ($Q \geq K$) until Q returns to the same value as K. This process is described by Le Chatelier's principle.

Le Chatelier's principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> *A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.*

The stress on the system in Figure **7.1.6.1** is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.

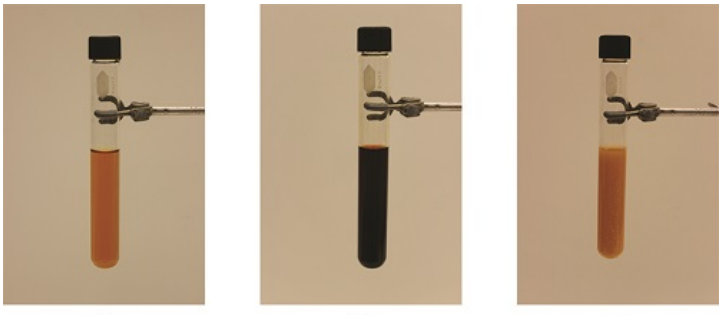


Figure* 7.1.6.1*: *(a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN. $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott).*

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)} \tag{7.1.6.1}$$

$$K_c = 50.0 \text{ at } 400^\circ\mathrm{C} \tag{7.1.6.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[\mathrm{H_2}] = [\mathrm{I_2}] = 0.221\ M$ and $[\mathrm{HI}] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If $\mathrm{H_2}$ is introduced into the system so quickly that its concentration doubles before it begins to react (new $[\mathrm{H_2}] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[\mathrm{H_2}] = 0.374\ M$,
- $[\mathrm{I_2}] = 0.153\ M$, and
- $[\mathrm{HI}] = 1.692\ M$.

This gives:

$$\begin{aligned} Q_c &= \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} \\ &= \frac{(1.692)^2}{(0.374)(0.153)} \\ &= 50.0 = K_c \end{aligned}$$

We have stressed this system by introducing additional $\mathrm{H_2}$. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess $\mathrm{H_2}$, reducing the amount of uncombined $\mathrm{I_2}$, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, $\mathrm{O_2}$, and $\mathrm{NO_2}$ are at equilibrium:

$$\mathrm{2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)} \tag{7.1.6.3}$$

The formation of additional amounts of $\mathrm{NO_2}$ decreases the total number of molecules in the system because each time two molecules of $\mathrm{NO_2}$ form, a total of three molecules of NO and $\mathrm{O_2}$ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of $\mathrm{NO_2}$ into NO and $\mathrm{O_2}$, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{7.1.6.4}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4\ kJ\ (exothermic)} \tag{7.1.6.5}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + heat} \tag{7.1.6.6}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ in this reaction

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20\ kJ} \tag{7.1.6.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{7.1.6.8}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathrm{NO_2}$ molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless $\mathrm{N_2O_4}$ increases, and the concentration of brown $\mathrm{NO_2}$ decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equlibrium properties is tabulated in Table 7.1.6.1.

Table 7.1.6.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Example 7.1.6.1

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + \mathbf{O_{2(g)}}$: the amount of HgO is doubled.
b. $NH_4HS_{(s)} \rightleftharpoons \mathbf{NH_{3(g)}} + H_2S_{(g)}$: the concentration of H_2S is tripled.
c. $\mathbf{n\text{-}butane}_{(g)} \rightleftharpoons isobutane_{(g)}$: the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

Because $HgO_{(s)}$ and $Hg_{(l)}$ are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2, so no compensatory change is necessary.

NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K.

For this reaction, $K = \frac{[isobutane]}{[n\text{-}butane]}$, so halving the concentration of isobutane means that the n-butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise 7.1.6.1

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

a. $\mathbf{HBr(g)} + \mathrm{NaH(s)} \rightleftharpoons \mathrm{NaBr(s)} + \mathbf{H_2(g)}$: the concentration of **HBr** is decreased by a factor of 3.

b. $6\,Li\,(s) + N_2(g) \rightleftharpoons 2\,Li_3N\,(s)$: the amount of Li is tripled.
c. $SO_2(g) + Cl_2\,(g) \rightleftharpoons SO_2Cl_2\,(l)$: the concentration of Cl_2 is doubled.

Answer a

$K = \frac{[H_2]}{[HBr]}$; $[H_2]$ must decrease by about a factor of 3.

Answer b

$K = \frac{1}{[N_2]}$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.

Answer c

$K = \frac{1}{[SO_2][Cl_2]}$; $[SO_2]$ must decrease by about half.

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations. The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \tag{7.1.6.9}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements (Equation 7.1.6.9). The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.



Figure 7.1.6.1: The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable to a majority of plants due the tremendous stability of the nitrogen-nitrogen triple bond.

Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

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CHAPTER OVERVIEW

7.2: Introduction to Acid–Base Equilibria

Acids and bases have been defined differently by three sets of theories. One is the Arrhenius definition, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. On the other hand, the Bronsted-Lowry definition defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons. Also, the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors. Acids and bases can be defined by their physical and chemical observations.

7.2.1: Brønsted–Lowry Acids and Bases

7.2.2: Autoionization of Water

7.2.3: pH and pOH

7.2.4: Acid Strength

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7.2.1: Brønsted–Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Describe the acid-base behavior of amphiprotic substances
- Understand acid-base reactivity as a proton transfer process.

In previous chapters, we have understood acids and bases in terms of the Arrhenius definition: an acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base is a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. In this chapter, we will extend the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base.

Table 7.2.1.1: Definitions of Acids and Bases

Definition	Acid	Base
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor

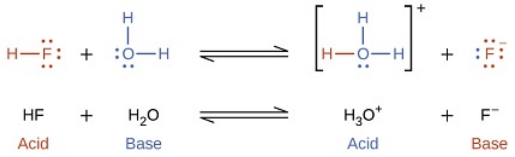
Brønsted-Lowry Acids

Brønsted-Lowry acids may be neutral molecules such as HCl, H_2SO_4, or acetic acid (CH_3COOH). Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. In general, we can symbolize any acid as HA and describe the donation of a proton to a water molecule as follows:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \tag{7.2.1.1}$$

We call the product, A^-, that remains after an acid donates a proton the **conjugate base** of the acid. In the generalized example above, the anion (A^-) is the conjugate base of the acid (HA). This species is called a base because it can accept a proton (to re-form the original acid).

The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are donated from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

The fluoride ion (F^-) is the conjugate base of hydrofluoric acid (HF). Here are several other examples of acid ionization in water:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^- \tag{7.2.1.2}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3 \tag{7.2.1.3}$$

In each case, the acid ionization process results in the formation of the conjugate base! Identifying **acid-base conjugate pairs** will help you understand acid-base reactivity.

Example 7.2.1.1: Conjugate Acid-Base Pairs

Identify the conjugate base for each of the following acids:

a) acetic acid ($HC_2H_3O_2$)

b) hydrocyanic acid (HCN)

c) phosphoric acid (H_3PO_4)

Solution

a) $C_2H_3O_2^-$

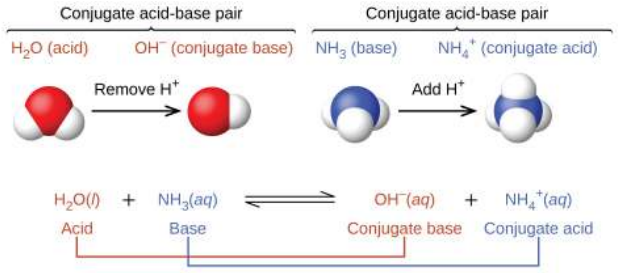
b) CN^-

c) $H_2PO_4^-$

Brønsted-Lowry Bases

Brønsted-Lowry bases may, likewise, be neutral molecules (such as NH_3 and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-.

When we add a base to water, a base ionization reaction occurs in which a proton is transferred from a water molecule and accepted by the base molecule (or ion). For example, adding ammonia to water yields hydroxide ions and ammonium ions. We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base).



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter.

Acid-Base Reactions

Acid-base reactivity under the Brønsted-Lowry definition can be considered a **proton transfer** process. In this process the proton is transferred from the acid to the base. Consider the following reaction between hydrocyanic acid (HCN) and ammonia (NH_3):

Example 7.2.1.2: Acid-Base Reaction (Proton Transfer)

Write and equation for the reaction that would occur between hydrocyanic acid (HCN) and ammonia (NH_3).

Solution

This is a proton transfer reaction. The acid will donate a proton and the base will accept a proton.

$$HCN(aq) + NH_3(aq) \rightleftharpoons CN^-(aq) + NH_4^+(aq)$$

Amphiprotic Species

Many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act

either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \quad (7.2.1.4)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \quad (7.2.1.5)$$

Example 7.2.1.3: The Acid-Base Behavior of an AmphoPROTIC Substance

Write separate equations representing the ionization in water of HSO_3^-

a. as an acid
b. as a base

Solution

a. $HSO_3^-(aq) + H_2O(aq) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$
b. $HSO_3^-(aq) + H_2O(aq) \rightleftharpoons H_2SO_3(aq)^+ \ OH^-(aq)$

Exercise 7.2.1.1

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

Answer b

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O_{(l)}$$

In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. The amphoprotic nature of water plays a central role in aqueous acid-base reactivity and will be discussed further in the next section.

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is an important amphiprotic species.

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

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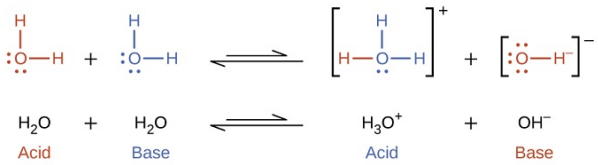
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7.2.2: Autoionization of Water

Learning Objectives

- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations

In the preceding section we saw that water is an amphiprotic substance. It can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O\,(l) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + OH^-\,(aq)} \quad K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{7.2.2.1}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

Example 7.2.2.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$. At 25 °C:

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = [\mathrm{H_3O^+}]^{2+} = [\mathrm{OH^-}]^{2+} = 1.0 \times 10^{-14} \tag{7.2.2.2}$$

So:

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M \tag{7.2.2.3}$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 7.2.2.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the value of the equilibrium constant. The following example demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations in an aqueous solution.

Example 7.2.2.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{7.2.2.4}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{7.2.2.5}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9} \tag{7.2.2.6}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14} \tag{7.2.2.7}$$

Exercise 7.2.2.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M \tag{7.2.2.8}$$

Summary

Water is an important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{7.2.2.9}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_2O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C \tag{7.2.2.10}$$

{Key Equations

- $$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25 °C)} \tag{7.2.2.11}$$

Glossary

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

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7.2.3: pH and pOH

Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{7.2.3.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{7.2.3.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{7.2.3.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{7.2.3.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{7.2.3.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{7.2.3.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{7.2.3.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{7.2.3.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{7.2.3.9}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{7.2.3.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{7.2.3.11}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Table 7.2.3.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 7.2.3.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

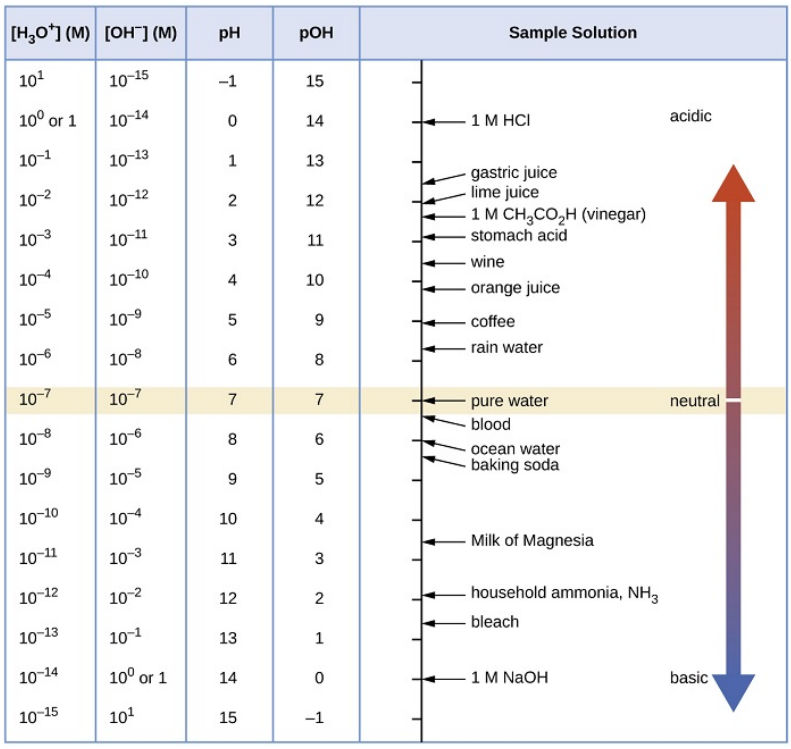


Figure 7.2.3.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 7.2.3.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 7.2.3.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 7.2.3.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3$$

$$\log[\mathrm{H_3O^+}] = -7.3$$

$$[\mathrm{H_3O^+}] = 10^{-7.3}$$

or

$$[\mathrm{H_3O^+}] = \text{antilog of} -7.3$$

$$[\mathrm{H_3O^+}] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 7.2.3.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

"Neutral" doesn't always mean $pH = 7$!

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[\mathrm{H_3O^+}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

$$\begin{aligned} pOH &= -\log[\mathrm{OH^-}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 7.2.3.1).

THE PH SCALE DOES NOT HAVE UPPER NOR LOWER BOUNDS!

It is common that the pH scale is argued to range from 0-14 or perhaps 1-14, but neither is correct. The pH range does not have an upper nor lower bound, since as defined above, the pH is an indication of concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Hence a range of 0

to 14 provides sensible (but not absolute) "bookends" for the scale. One can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar.

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{7.2.3.12}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{7.2.3.13}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{7.2.3.14}$$

$$\mathrm{H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)} \tag{7.2.3.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure **7.2.3.2**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



(a) (b)

Figure **7.2.3.2**: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

Example **7.2.3.3**: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125$ M:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log 0.0125 \tag{7.2.3.16}$$

$$= -(-1.903) = 1.903 \tag{7.2.3.17}$$

The pH can be found from the **pOH**:

$$\mathrm{pH} + \mathrm{pOH} = 14.00 \tag{7.2.3.18}$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10 \tag{7.2.3.19}$$

Exercise 7.2.3.3

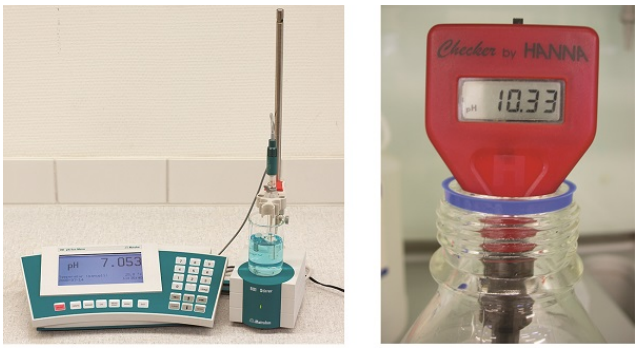
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 7.2.3.3).



(a) (b)

Figure 7.2.3.3: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 7.2.3.3).



(a) (b)

Figure 7.2.3.4: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$
- $\mathrm{pOH} = -\log[\mathrm{OH^-}]$

- $[H_3O^+] = 10^{-pH}$
- $[OH^-] = 10^{-pOH}$
- $pH + pOH = pK_w = 14.00$ at 25 °C

Glossary

acidic
describes a solution in which $[H_3O^+] > [OH^-]$

basic
describes a solution in which $[H_3O^+] < [OH^-]$

neutral
describes a solution in which $[H_3O^+] = [OH^-]$

pH
logarithmic measure of the concentration of hydronium ions in a solution

pOH
logarithmic measure of the concentration of hydroxide ions in a solution

Contributors and Attributions

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7.2.4: Acid Strength

Learning Objectives

- Assess the relative strengths of acids according to their ionization constants
- Carry out equilibrium calculations for weak acid systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The ionization of an acid in water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{7.2.4.1}$$

In the ionization process, water acts as the base accepting a proton from the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion ($\mathrm{H_3O^+}$) is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water. Table 7.2.4.1 lists several strong acids. A weak acid does not completely ionize in water, yielding only small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Table 7.2.4.1: Some of the common strong acids and bases are listed here.

Common Strong Acids		Common Strong Bases	
$\mathrm{HClO_4}$	perchloric acid		
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ba(OH)_2}$	barium hydroxide
$\mathrm{HNO_3}$	nitric acid		
$\mathrm{H_2SO_4}$	sulfuric acid		

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant, K_a**. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{7.2.4.2}$$

we write the equation for the ionization constant as:

$$K_a = \frac{[H3O+][A-]}{[HA]} \tag{7.2.4.3}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include [H_2O] in the equation. The larger the K_a of an acid, the larger the concentration of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the nonionized acid, HA at equilibrium. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\begin{aligned} \mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_a = 1.8 \times 10^{-5} \\ \mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_a = 4.6 \times 10^{-4} \\ \mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(aq) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_a = 1.2 \times 10^{-2} \end{aligned} \tag{7.2.4.4}$$

Table 7.2.4.2 gives the ionization constants for several weak acids; additional ionization constants can be found in Reference Table E1.

Table 7.2.4.2: Ionization Constants of Some Weak Acids

Acid	K_a at 25 °C
H_2SO_3	1.5×10^{-2}
HSO_4^-	1.2×10^{-2}
H_3PO_4	7.5×10^{-3}
HF	3.5×10^{-4}
HNO_2	4.6×10^{-4}
HNCO	2×10^{-4}
HCO_2H	1.8×10^{-4}
$HC_3H_5O_3$	1.4×10^{-4}
$HC_2H_3O_2$	1.8×10^{-5}
H_2CO_3	4.3×10^{-7}
HSO_3^-	1.0×10^{-7}
H_2S	9.1×10^{-8}
HClO	3.5×10^{-8}
HBrO	2.0×10^{-9}
HCN	6.2×10^{-10}
NH_4^+	5.6×10^{-10}
HCO_3^-	4.8×10^{-11}
H_2O_2	2.4×10^{-12}
H_2O	1.0×10^{-14}

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\% \text{ ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{7.2.4.5}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 7.2.4.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100 \tag{7.2.4.6}$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq). \tag{7.2.4.7}$$

Since $10^{-\text{pH}} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 7.2.4.5) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\% \tag{7.2.4.8}$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 7.2.4.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \tag{7.2.4.9}$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base **B**, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Table 7.2.4.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

The extent to which an acid, HA, donates protons to water molecules is relative to the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. However, if A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases.

Figure 7.2.4.1 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 7.2.4.1 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 7.2.4.1 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 7.2.4.1 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

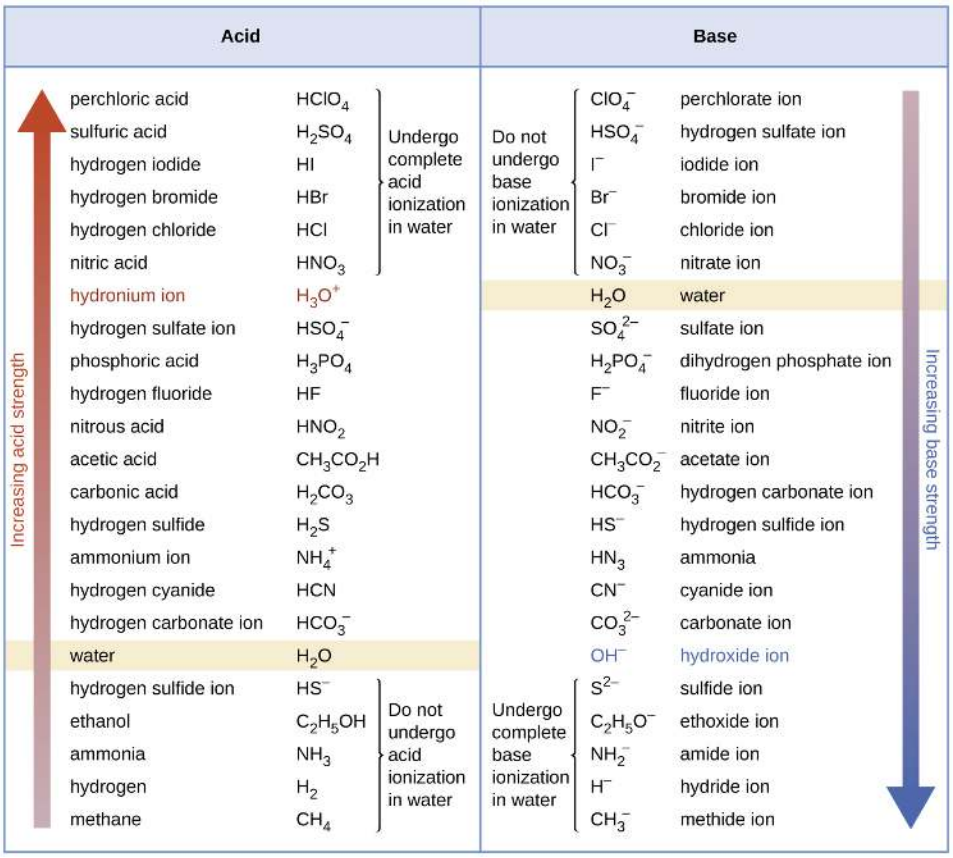


Figure **7.2.4.1**: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure **7.2.4.1**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Exercise 7.2.4.2

We can determine the relative acid strengths of $\mathbf{NH_4^+}$ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of $\mathbf{NH_4^+}$ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of $\mathbf{NH_4^+}$, and decide which is the stronger acid, HCN or $\mathbf{NH_4^+}$.

Answer

$\mathbf{NH_4^+}$ is the slightly stronger acid (K_a for $\mathbf{NH_4^+} = 5.6 \times 10^{-10}$).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid ($\mathbf{CH_3CO_2H}$) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq) \qquad (7.2.4.10)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure **7.2.4.2**). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = 1.8 \times 10^{-5} \tag{7.2.4.11}$$



Figure **7.2.4.2**: pH paper indicates that a 0.l-M solution of **HCl** (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = *0.1 M. A 0.1-M solution of* CH_3CO_2H *(beaker on right) has a pH of 3 (* $[H_3O^+]$ *= 0.001 M) because the weak acid* CH_3CO_2H *is only partially ionized. In this solution,* $[H_3O^+] < [CH_3CO_2H]$. *(credit: modification of work by Sahar Atwa)*

Example 7.2.4.2: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \tag{7.2.4.12}$$

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5} \tag{7.2.4.13}$$

Exercise 7.2.4.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \tag{7.2.4.14}$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Example 7.2.4.3: Determination of K_a from pH

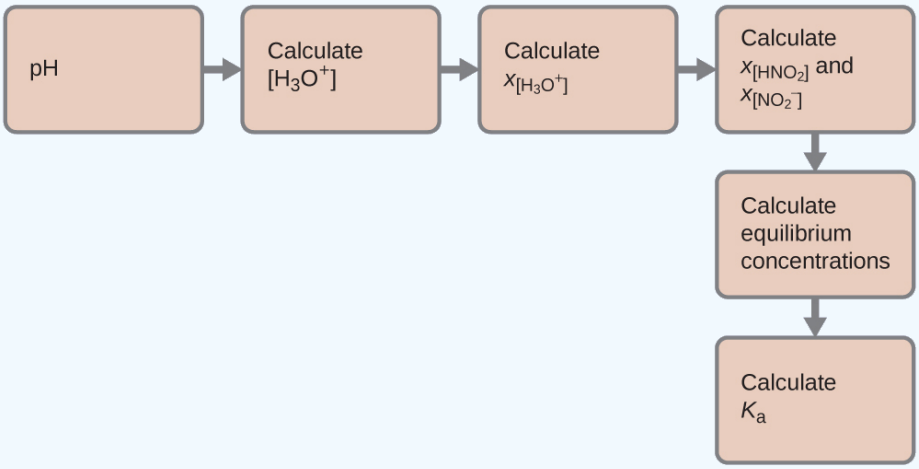
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \tag{7.2.4.15}$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−*x*	+ *x*	*x*
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) =$ 0.0516 + (−*x*)	$[H_3O]^+ + x[NO_2]^-$ + *x* ~0 + *x*	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M \tag{7.2.4.16}$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 +	H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−*x*	+	*x* = 0.0046	*x* = 0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H3O+][NO2-]}{[HNO2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4} \tag{7.2.4.17}$$

Example 7.2.4.4: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4} \tag{7.2.4.18}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \tag{7.2.4.19}$$

The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H3O+][HCO2-]}{[HCO2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for *x*. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534} \tag{7.2.4.20}$$

Solve for *x* as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4}) = 9.6 \times 10^{-5} \tag{7.2.4.21}$$
$$x = \sqrt{9.6 \times 10^{-5}}$$
$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$
$$= 1.8 \times 10^{-2} (1.8$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[H_3O^+] = \ 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$
$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 7.2.4.4: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \quad K_a = 1.8 \times 10^{-5} \tag{7.2.4.22}$$

Hint

Determine $[CH_3CO_2{}^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Answer

percent ionization = 1.3%

Some weak acids ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

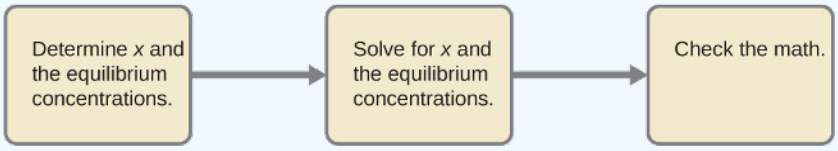
Example 7.2.4.5: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the $HSO_4{}^-$ ion, a weak acid. What is the pH of a 0.50-*M* solution of $HSO_4{}^-$?

$$HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4{}^{2-}(aq) \quad K_a = 1.2 \times 10^{-2} \tag{7.2.4.23}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of $HSO_4{}^-$ so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌ H_3O^+ + SO_4^{2-}			
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$		$0 + x = x$	$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for *x*, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of *x*.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2}-]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x} \tag{7.2.4.24}$$

If we assume that *x* is small and approximate (0.50 − *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2} \tag{7.2.4.25}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05 \tag{7.2.4.26}$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%) \tag{7.2.4.27}$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x} \tag{7.2.4.28}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^{2+} \tag{7.2.4.29}$$

or

$$x^{2+} + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0 \tag{7.2.4.30}$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0, \tag{7.2.4.31}$$

x is given by the equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a} \tag{7.2.4.32}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2} \tag{7.2.4.33}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[\mathrm{H_3O^+}] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 7.2 \times 10^{-2} = 1.14 \tag{7.2.4.34}$$

Summary

The strengths of Brønsted-Lowry acids in aqueous solutions can be determined by their acid ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion.

Key Equations

- $K_a = \dfrac{[H3O+][A-]}{[HA]}$
- $\text{Percent ionization} = \dfrac{[H3O+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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SECTION OVERVIEW

Topic H - Condensed States and Attractive Forces Between Particles

Learning Objectives

WHAT YOU SHOULD BE ABLE TO DO WHEN YOU HAVE FINISHED THIS TOPIC:

1. Compare/contrast the qualitative properties of three states of matter: solid, liquid, gas
2. Know the two factors that determine the physical state of matter.
3. Know how average kinetic energy of the particles changes with temperature.
4. Know the types and relative strengths of attractive forces between particles.
5. Relate the physical properties of substances to the attractive forces between particles:
    a. For solids: melting point, malleability, ductility, conductivity, solubility in water
    b. For liquids: boiling point, surface tension, viscosity, vapor pressure, solubility in water
6. Know the four types of solids (molecular, ionic, metallic, network covalent) and categorize individual substances based on their physical behavior.
7. Sketch and interpret a typical phase diagram for a pure substance, including identification of the triple point and the critical point.
8. Construct a Born-Haber diagram given appropriate energy values, and calculate any of the individual energy values where appropriate.

8.1: Condensed States and Intermolecular Forces

8.1.1: A Molecular Comparison of Gases, Liquids, and Solids
8.1.2: Intermolecular Forces
8.1.3: Properties of Liquids
8.1.4: Properties of Solids
8.1.5: Phase Changes
8.1.6: Phase Diagrams
8.1.7: The Born-Haber Cycle

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CHAPTER OVERVIEW

8.1: Condensed States and Intermolecular Forces

The physical properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same chemical properties, but their physical properties are considerably different. In general Covalent bonds determine: molecular shape, bond energies, chemical properties, while intermolecular forces (non-covalent bonds) influence the physical properties of liquids and solids. The kinetic molecular theory of gases described in an earlier chapter gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

8.1.1: A Molecular Comparison of Gases, Liquids, and Solids
8.1.2: Intermolecular Forces
8.1.3: Properties of Liquids
8.1.4: Properties of Solids
8.1.5: Phase Changes
8.1.6: Phase Diagrams
8.1.7: The Born-Haber Cycle

Thumbnail: A water drop. (CC BY 2.0; José Manuel Suárez).

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8.1.1: A Molecular Comparison of Gases, Liquids, and Solids

Learning Objectives

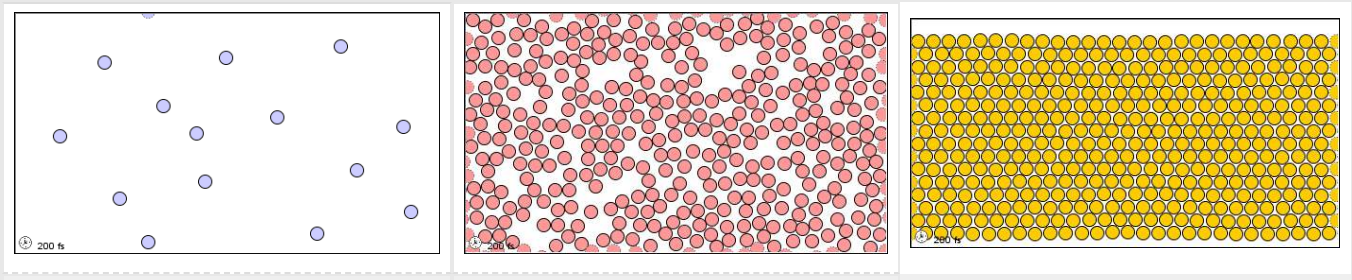
- To be familiar with the kinetic molecular description of gases, liquids, and solids.

The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *Covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.



Figure **8.1.1.1**: Three fundamental states of matter: gas, liquid, and solid. These states are represented, left to right, the air around clouds, a drop of water, and an ice sculpture, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance and the intermolecular forces try to draw the particles together (Figure **8.1.1.2**). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces



(a) in the gaseous state	*(b) as a liquid*	(c) *in solid form*

Figure **8.1.1.2**: Molecular level picture of gases, liquids and solids.

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container
- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

> *Thus, liquids can be poured and assume the shape of their containers*

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

> *Due to the strong intermolecular forces between neighboring molecules, solids are rigid*

- Cooling a gas may change the state to a liquid
- Cooling a liquid may change the state to a solid
- Increasing the pressure on a gas may change the state to a liquid
- Increasing the pressure on a liquid may change the state to a solid



Video **8.1.1.1**: Video highlighting the properties for the three states of matter. Source found at https://www.youtube.com/watch?v=s-KvoVzukHo.

Physical Properties of Liquids

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described previously This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers. A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces. Solids and liquids have particles that are fairly close to one another, and are thus called "**condensed phases**" to distinguish them from gases

- **Density**: The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore

more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.

- **Molecular Order:** Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids, the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.
- **Compressibility**: Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.
- **Thermal Expansion**: The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table S1 (with a shorten version in Table **8.1.1.1**) that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table **8.1.1.1**: The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.
- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure **8.1.1.3**).

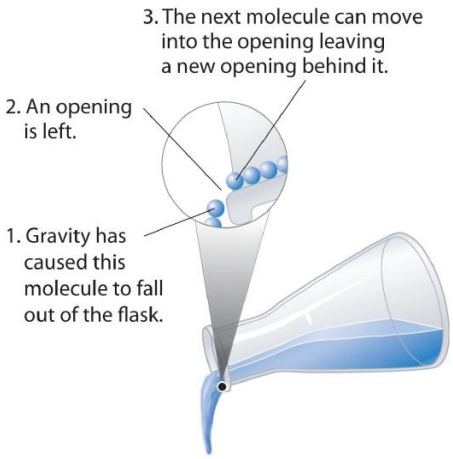


Figure **8.1.1.3**: Why Liquids Flow. Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container. (CC BY-SA-NC; Anonymous vy request).

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8.1.2: Intermolecular Forces

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids but are more similar to solids.*

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law,.)

In this section, we explicitly consider three kinds of intermolecular interactions: There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure **8.1.2.1*a***.

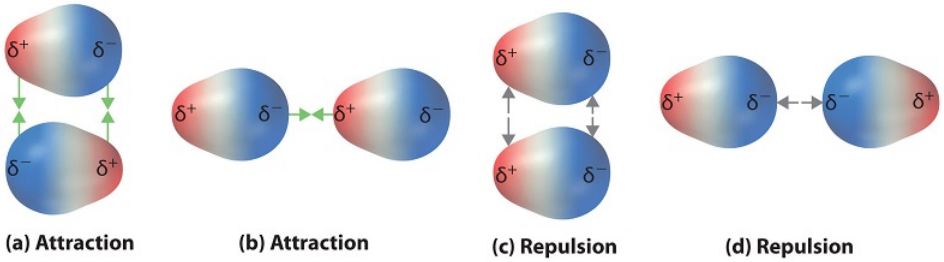


Figure **8.1.2.1**: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 8.1.2.1*c*). Hence dipole–dipole interactions, such as those in Figure 8.1.2.1*b*, are *attractive intermolecular interactions*, whereas those in Figure 8.1.2.1*d* are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 8.1.2.2. On average, however, the attractive interactions dominate.

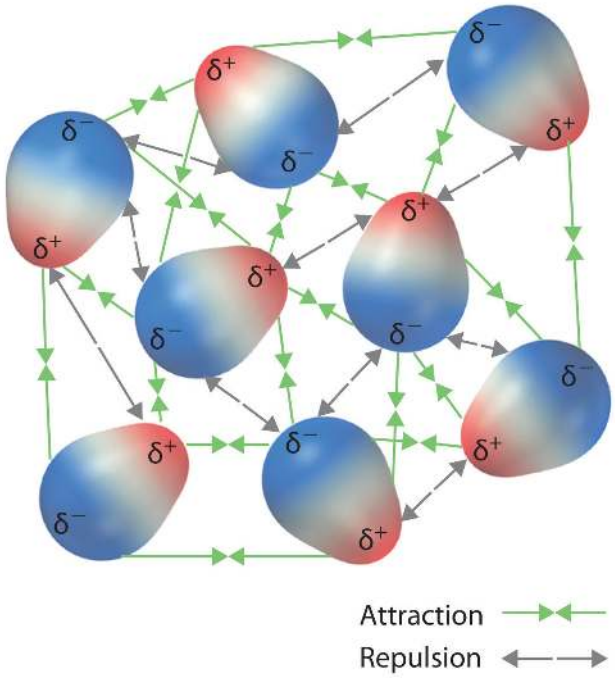


Figure* 8.1.2.2*: *Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules*

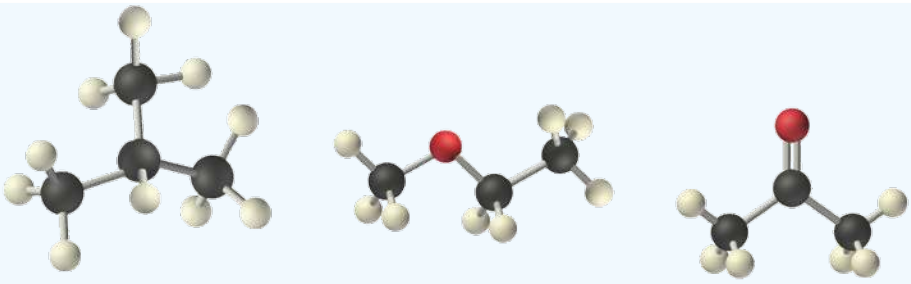
Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 8.1.2.1.

Table 8.1.2.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	

Example 8.1.2.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone.

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 8.1.2.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 8.1.2.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table **8.1.2.2**: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure **8.1.2.3**, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another.

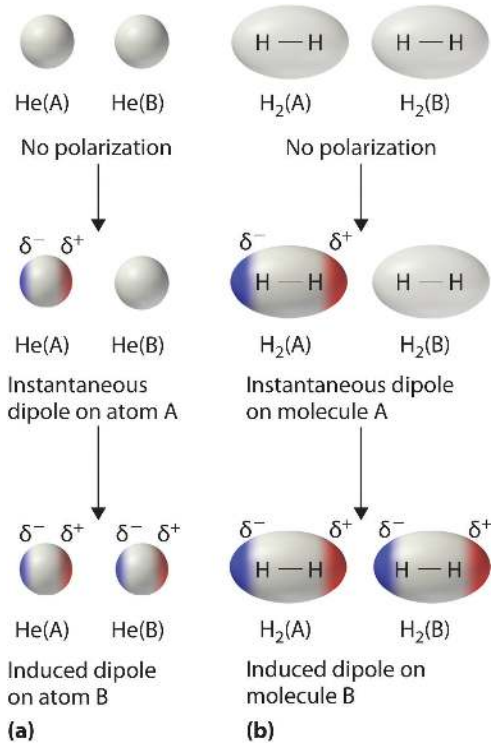


Figure **8.1.2.3**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure **8.1.2.3**, tends to become more pronounced as atomic and molecular masses increase (Table **8.1.2.2**). For example, Xe boils at

−108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 8.1.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 8.1.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

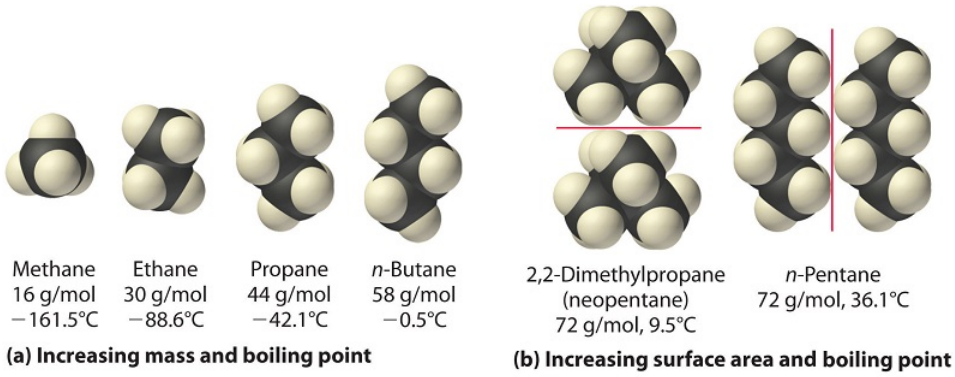


Figure 8.1.2.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 8.1.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise 8.1.2.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure **8.1.2.5**. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

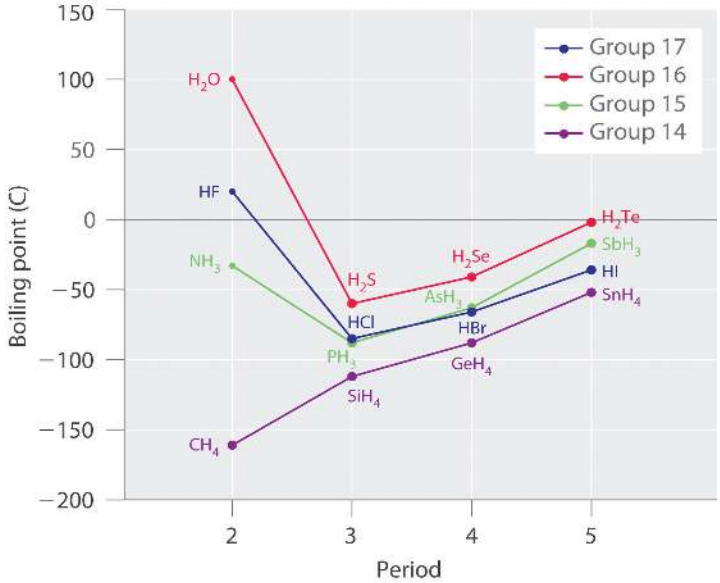


Figure **8.1.2.5**: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole

distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure **8.1.2.6**. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

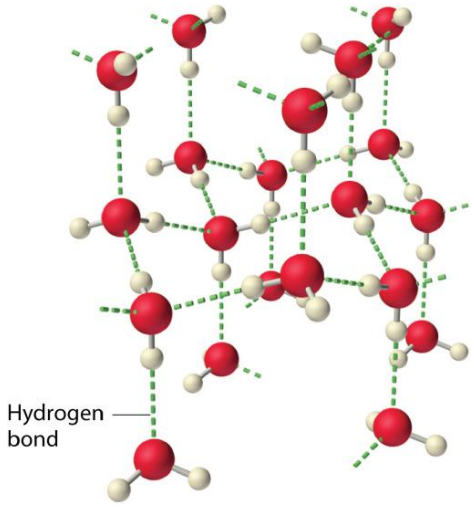


Figure* 8.1.2.6*: *The Hydrogen-Bonded Structure of Ice.*

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 8.1.2.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

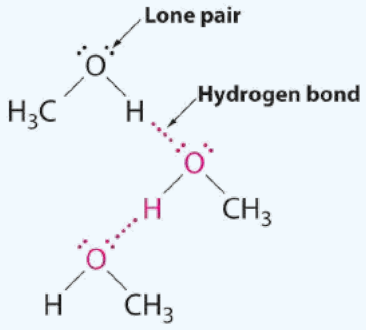
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



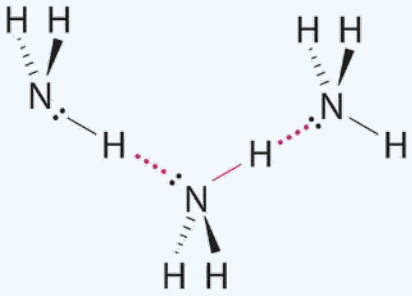
Hydrogen bonding in methanol

Exercise 8.1.2.3

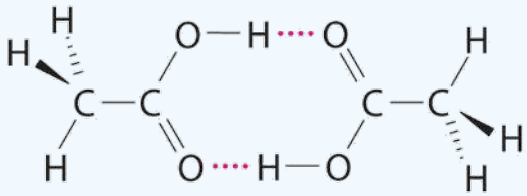
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 8.1.2.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269^\circ\text{C}) < \text{Ar } (-185.7^\circ\text{C}) < N_2O\ (-88.5^\circ\text{C}) < C_{60}\ (>280^\circ\text{C}) < \text{NaCl } (1465^\circ\text{C}).$$

Exercise 8.1.2.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Example 8.1.2.5:

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.

b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 8.1.2.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Summary

Molecules in liquids and solids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and decreases as the distance between dipoles increases. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

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8.1.3: Properties of Liquids

Learning Objectives

- To describe the unique properties of liquids: surface tension, capillary action, and viscosity.
- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action,
- viscosity, and
- vapor pressure.

Surface Tension

If liquids tend to adopt the shapes of their containers, then, do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29×10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86×10^{-1} J/m^2 (at 20°C).

Figure **8.1.3.1** presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

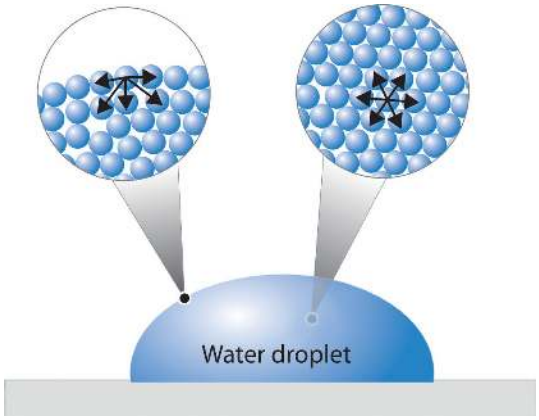


Figure **8.1.3.1**: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it "floats," even though steel is much denser

than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even observable in the zero gravity conditions of space as shown in Figure **8.1.3.2** (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!



***Figure* 8.1.3.2:** *The Effects of the High Surface Tension of Liquid Water. The full video can be found at https://www.youtube.com/watch?v=9jB7rOC5kG8.*

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table **8.1.3.1**. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table **8.1.3.1**: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure **8.1.3.3**. When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

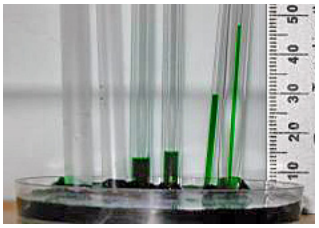


Figure* 8.1.3.3*: *The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.*

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure **8.1.3.4**). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure **8.1.3.4**).

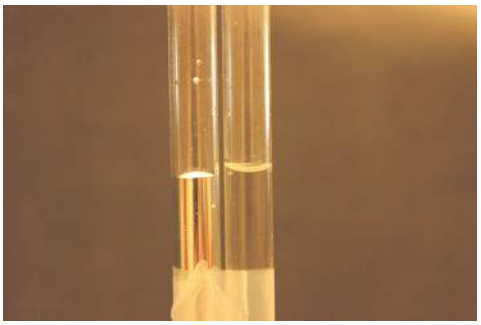


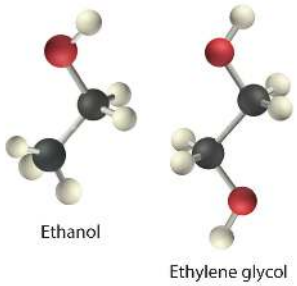
Figure* 8.1.3.4*: *The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)*

Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and "wick" the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become "tangled" with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too "thin" (have too low a viscosity) to be effective at high temperatures.



Figure 8.1.3.5: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure 8.1.3.5). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives "for improved engine performance" are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 8.1.3.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise 8.1.3.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 8.1.3.1), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

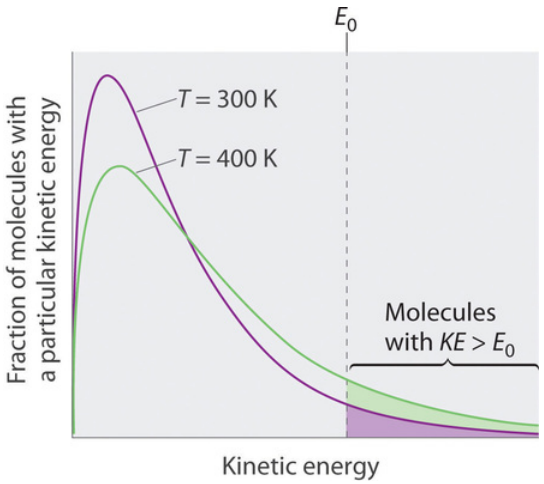


Figure 8.1.3.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 8.1.3.2. When a liquid is introduced into an evacuated chamber (part (a) in Figure 8.1.3.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

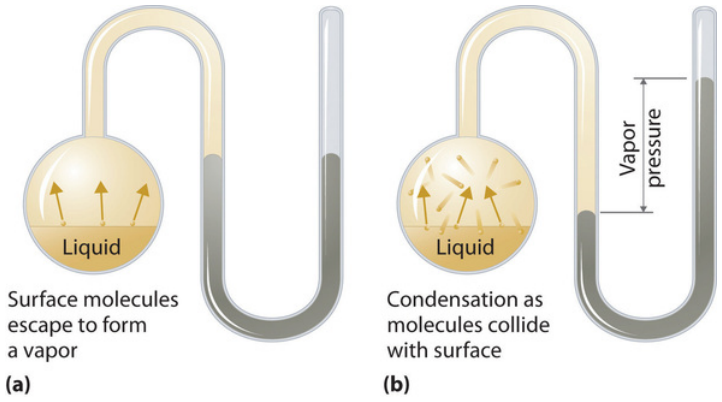


Figure **8.1.3.2**: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure **8.1.3.2**). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure **8.1.3.3**.

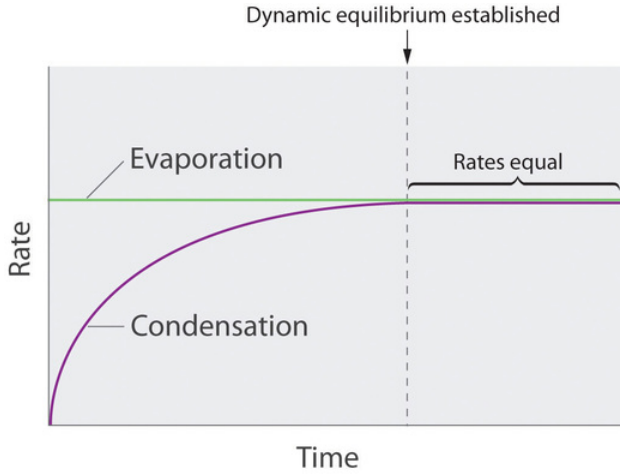


Figure **8.1.3.3**: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with

vapor pressures greater than that of water (Figure **8.1.3.4**) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

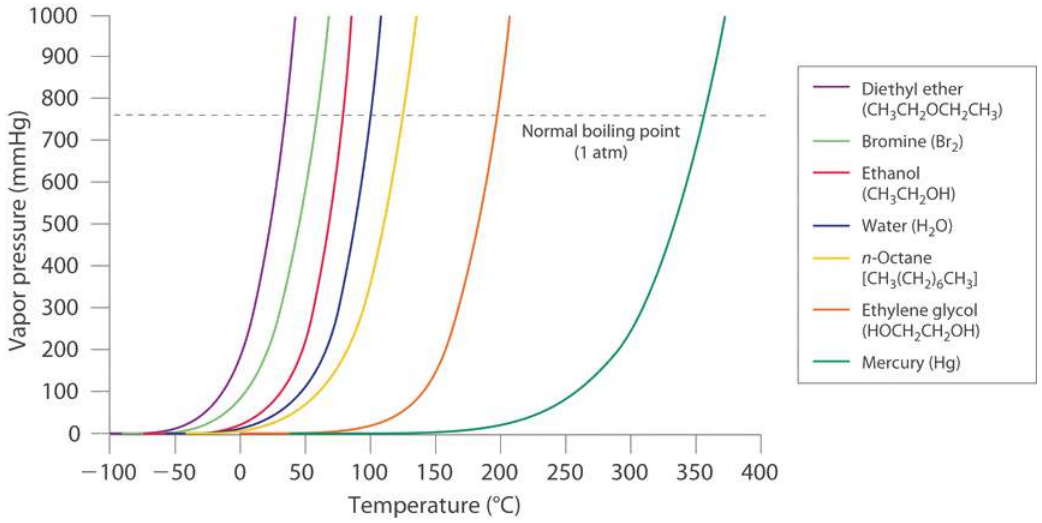


Figure **8.1.3.4**: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid.

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point (Table 11.4). It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure **8.1.3.4**. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure **8.1.3.4** are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table **8.1.3.1**: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table **8.1.3.1** lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

Example 8.1.3.2: Boiling Mercury

Use Figure **8.1.3.4** to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to https://www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure **8.1.3.4**, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure **8.1.3.4** and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

Exercise 8.1.3.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure **8.1.3.4** to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

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8.1.4: Properties of Solids

Learning Objectives

- To understand the correlation between bonding and the properties of solids.
- To classify solids as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions.

Crystalline solids fall into one of four categories. All four categories involve packing discrete molecules or atoms into a lattice or repeating array, though *network solids* are a special case. The categories are distinguished by the nature of the interactions holding the discrete molecules or atoms together. Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as ionic, molecular, covalent (network), or metallic. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Table **8.1.4.1**: Solids may be formally classified as ionic, molecular, covalent (network), or metallic

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High Melting Point, Brittle, Hard	NaCl, MgO
Molecular	Hydrogen Bonding, Dipole-Dipole, London Dispersion	Low Melting Point, Nonconducting	H_2, CO_2
Metallic	Metallic Bonding	Variable Hardness and Melting Point (depending upon strength of metallic bonding), Conducting	Fe, Mg
Network	Covalent Bonding	High Melting Point, Hard, Nonconducting	C (diamond), SiO_2 (quartz)

In ionic and molecular solids, there are no chemical bonds between the molecules, atoms, or ions. The solid consists of discrete chemical species held together by intermolecular forces that are **electrostatic** or **Coulombic** in nature. This behavior is most obvious for an ionic solid such as $NaCl$, where the positively charged Na^+ ions are attracted to the negatively charged Cl^- ions. Even in the absence of ions, however, electrostatic forces are operational. For polar molecules such as CH_2Cl_2, the positively charged region of one molecule is attracted to the negatively charged region of another molecule (dipole-dipole interactions). For a nonpolar molecule such as CO_2, which has no permanent dipole moment, the random motion of electrons gives rise to temporary polarity (a temporary dipole moment). Electrostatic attractions between two temporarily polarized molecules are called London Dispersion Forces.

Hydrogen bonding is a term describing an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. (See the IUPAC Provisional Recommendation on the definition of a hydrogen bond.) Dots are employed to indicate the presence of a hydrogen bond: X–H•••Y. The attractive interaction in a hydrogen bond typically has a strong electrostatic contribution, but dispersion forces and weak covalent bonding are also present.

In metallic solids and network solids, however, chemical bonds hold the individual chemical subunits together. The crystal is essential a single, macroscopic molecule with continuous chemical bonding throughout the entire structure. In metallic solids, the valence electrons are no longer exclusively associated with a single atom. Instead these electrons exist in molecular orbitals that are delocalized over many atoms, producing an electronic band structure. The metallic crystal essentially consists of a set of metal cations in a sea of electrons. This type of chemical bonding is called metallic bonding.

Ionic Solids

You learned previously that an ionic solid consists of positively and negatively charged ions held together by electrostatic forces. The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy** (i.e., the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase) is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

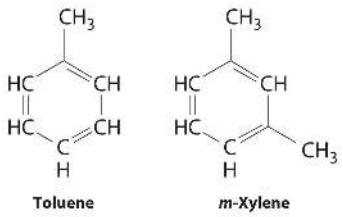
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these. The arrangement of the molecules in solid benzene is as follows:



The structure of solid benzene. In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles. (CC BY-NC-SA; Anonymous by request).

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and m-xylene [$m\text{-}C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene and m-xylene. The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene. (CC BY-NC-SA; Anonymous by request).

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure **8.1.4.1**, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.

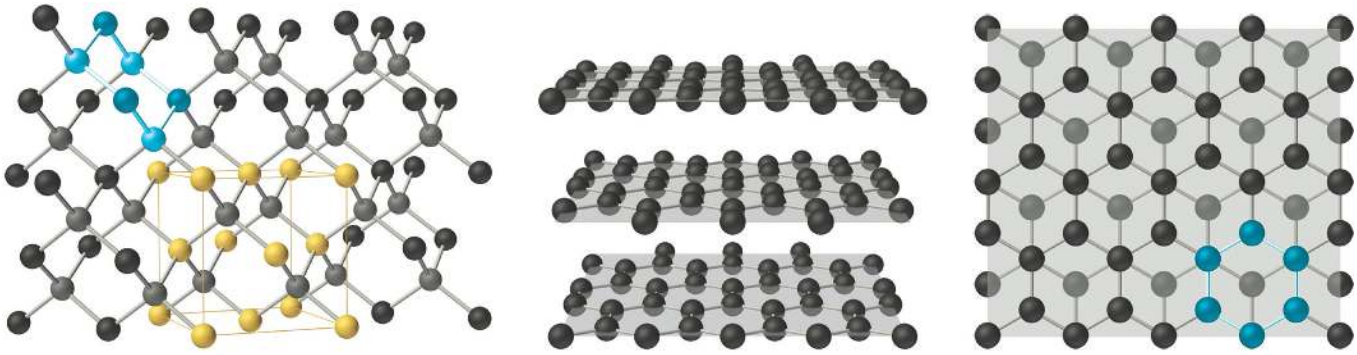


Figure **8.1.4.1**: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer. (CC BY-NC-SA; Anonymous by request).

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure **8.1.4.1**. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other

hand, is colorless when pure because it has no delocalized electrons. Table **8.1.4.2** compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table **8.1.4.2**: A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

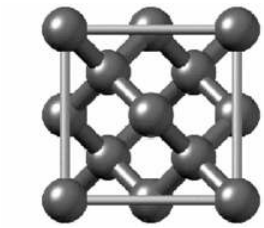


Figure **8.1.4.2**: Rotating model of diamond cubic. Figure used with permission from Wikipedia

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure **8.1.4.3** shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.

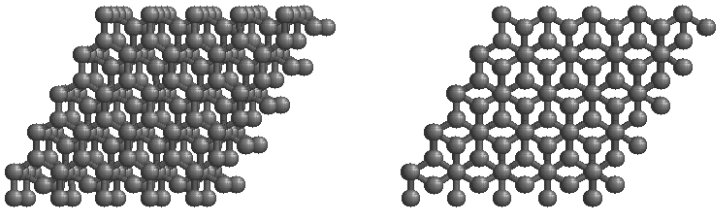


Figure 8.1.4.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoreticians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

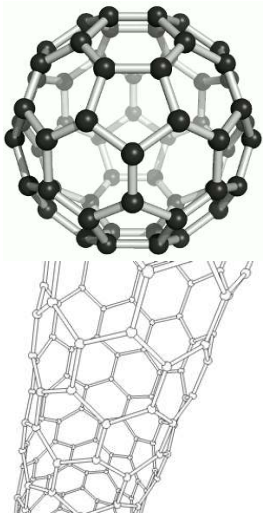


Figure 8.1.4.4: Example of fullerenes: a buckyball (*C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.*

The C_{60} molecule (Figure 8.1.4.4; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure 8.1.4.4; right). All of these substances are pure carbon.

Questions to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure **8.1.4.5**. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials.

Metals are characterized by their ability to reflect light, called luster, their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.

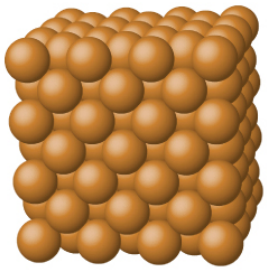


Figure* 8.1.4.5*: *Copper is a metallic solid. (CC BY; OpenStax).*

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

> *Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.*

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the d block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

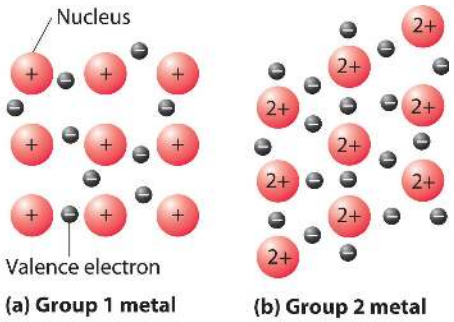


Figure **8.1.4.6**: The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron sea (Figure **8.1.4.6**). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. Some general properties of the four major classes of solids are summarized in Table **8.1.4.2**.

Table **8.1.4.2**: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

The general order of increasing strength of interactions in a solid is:

$$\textit{molecular solids} < \textit{ionic solids} \approx \textit{metallic solids} < \textit{covalent solids}$$

Example 8.1.4.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the p block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound C6(CH3)6 is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a d-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

Exercise 8.1.4.1

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer

C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C60, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. Covalent solids consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. Metallic solids have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compounds with unique properties.

Contributors and Attributions

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8.1.5: Phase Changes

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure **8.1.5.1**.

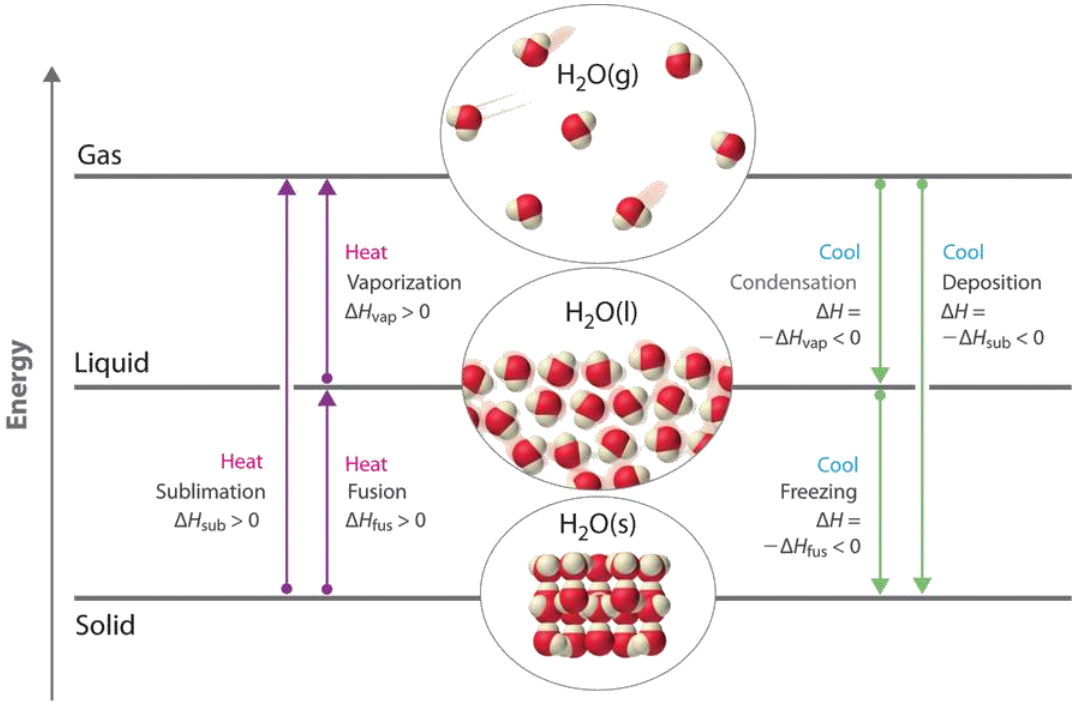


Figure **8.1.5.1**: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows.

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure **8.1.5.1**.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table **8.1.5.1**.

Table **8.1.5.1**: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

> *Less energy is needed to allow molecules to move past each other than to separate them totally.*



Figure **8.1.5.2**: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure **8.1.5.2**); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure **8.1.5.1**, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same T; this is an application of Hess's law.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{8.1.5.1}$$

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we

exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

The processes on the right side of Figure **8.1.5.1**—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure **8.1.5.3** shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

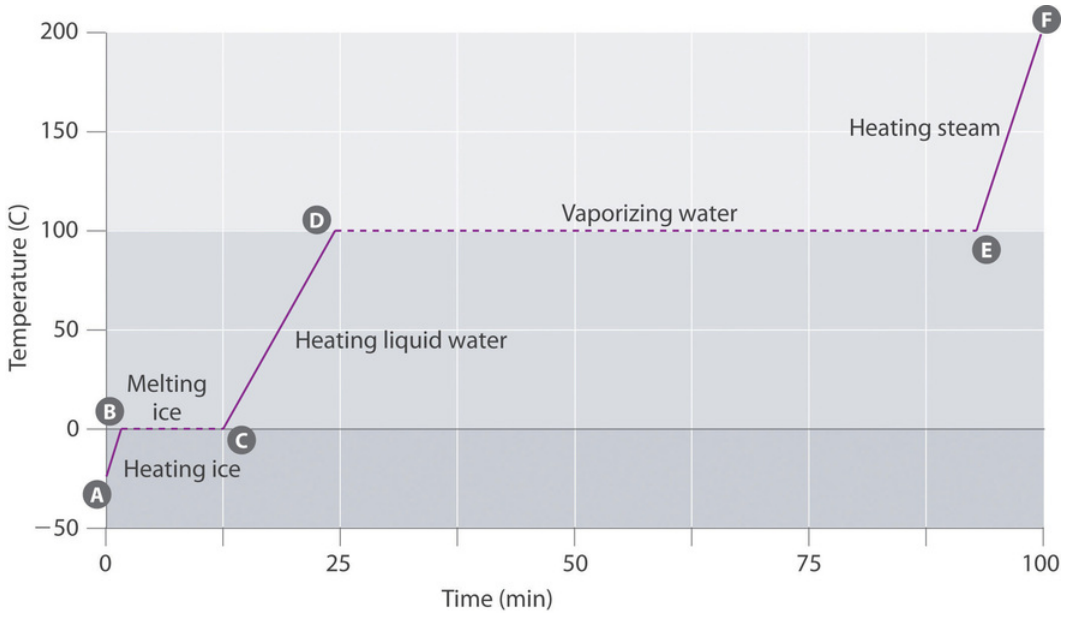


Figure **8.1.5.3**: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up

higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure **8.1.5.3**, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure **8.1.5.3**, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes "bumping" when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or "bump" the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a "boiling chip") in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure **8.1.5.4** plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure **8.1.5.3**, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

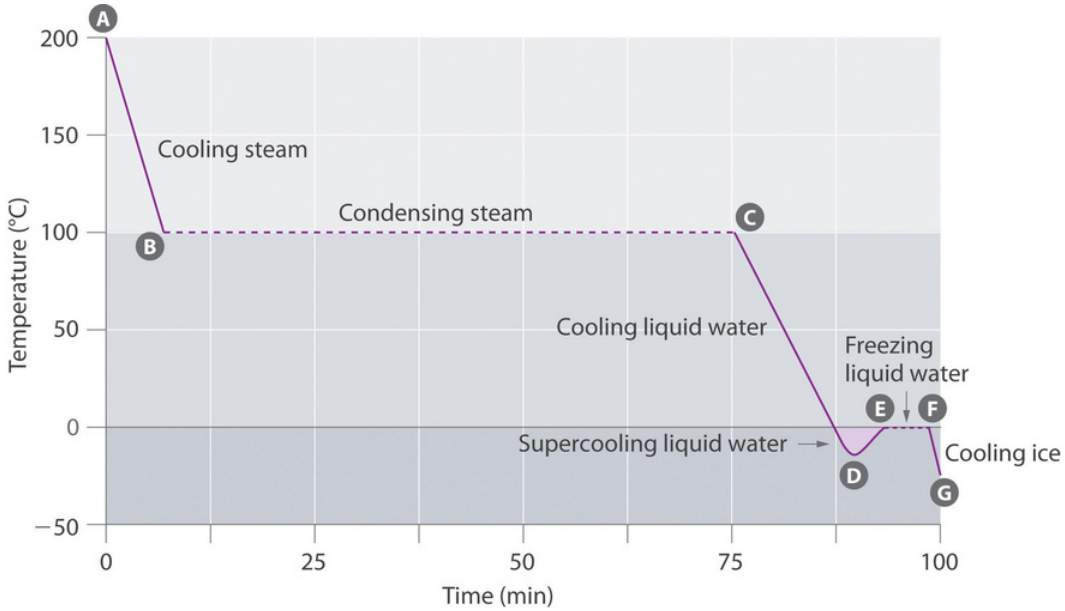


Figure **8.1.5.4**: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

Example 8.1.5.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T \tag{8.1.5.2}$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus} \tag{8.1.5.3}$$

For our 50.0 g ice cube:

$$q_{ice} = 50.0g \cdot \frac{1\,mol}{18.02\,g} \cdot 6.01\,kJ/mol = 16.7kJ \tag{8.1.5.4}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\,g}{1\,mL} \cdot 4.184J/(g\bullet°C)\Delta T \tag{8.1.5.5}$$

$$\Delta T = -7.98°C = T_f - T_i \tag{8.1.5.6}$$

$$T_f = 12.02°C \tag{8.1.5.7}$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$q_{ice} = -q_{tea} \tag{8.1.5.8}$$

$$q_{ice} = m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g \bullet °C) \cdot (T_f - 0.0°C) = 209.2J/°C \cdot T_f \tag{8.1.5.9}$$

$$\begin{aligned} q_{tea} = m_{tea}C_s\Delta T &= 500g \cdot 4.184J/(g \bullet °C) \cdot (T_f - 12.02°C) \\ &= 2092J/°C \cdot T_f - 25,150J \end{aligned} \tag{8.1.5.10}$$

$$209.2J/°C \cdot T_f = -2092J/°C \cdot T_f + 25,150J \tag{8.1.5.11}$$

$$2301.2J/°C \cdot T_f = 25,150J \tag{8.1.5.12}$$

$$T_f = 10.9°C \tag{8.1.5.13}$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

Exercise 8.1.5.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example **8.1.5.1**

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

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8.1.6: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure **8.1.6.1**). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure **8.1.6.1**) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

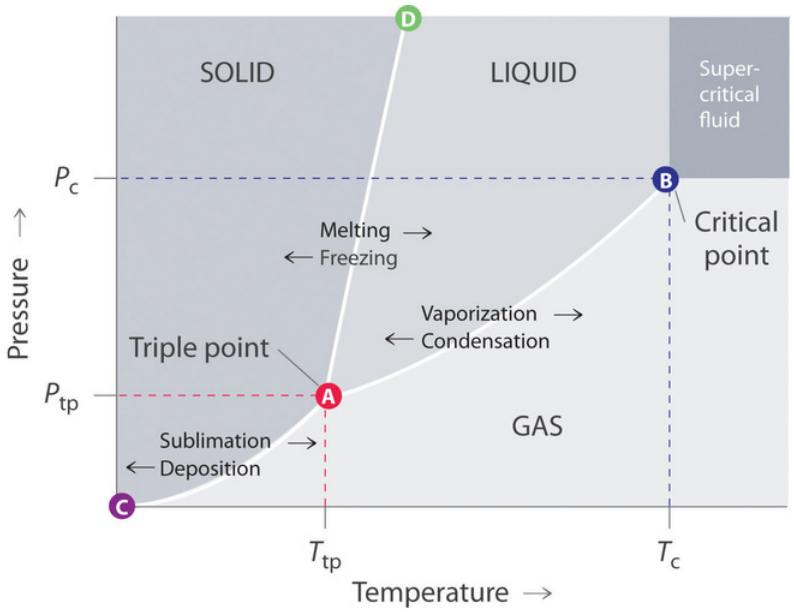


Figure* 8.1.6.1*: *A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region*

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure **8.1.6.1**, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 8.1.6.1, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 8.1.6.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

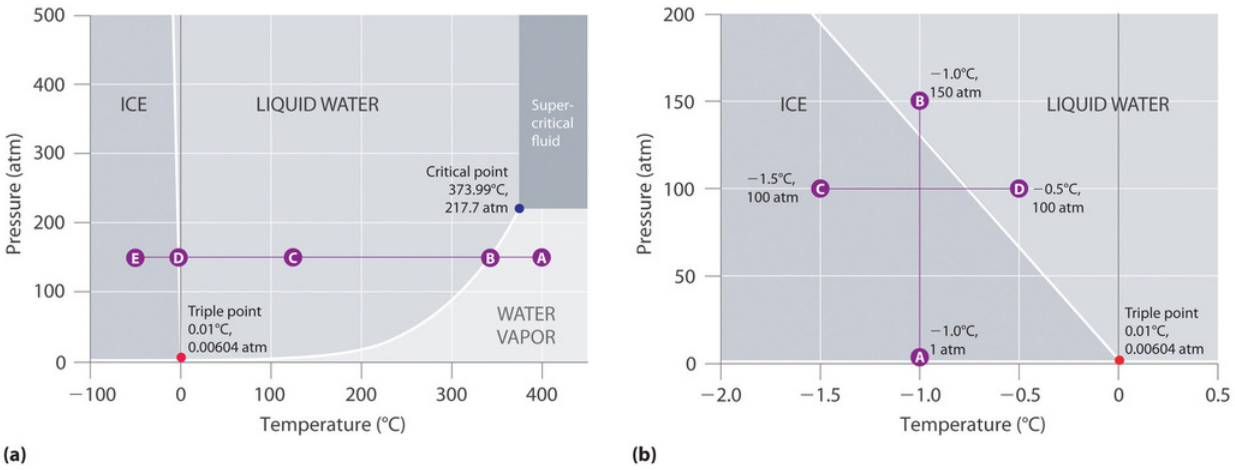


Figure 8.1.6.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 8.1.6.1).

The phase diagram for water illustrated in Figure 8.1.6.2*b* shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 8.1.6.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 8.1.6.2*b* point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.



Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (P) is the force (F) applied per unit area (A):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where m is the mass and g is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

Example 8.1.6.1: Water

Referring to the phase diagram of water in Figure **8.1.6.2**:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure **8.1.6.2**. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.
b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure **8.1.6.2**. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

Exercise 8.1.6.2

Referring to the phase diagram of water in Figure **8.1.6.2**, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure **8.1.6.3**) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



Dry ice ($\mathbf{CO_2(s)}$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

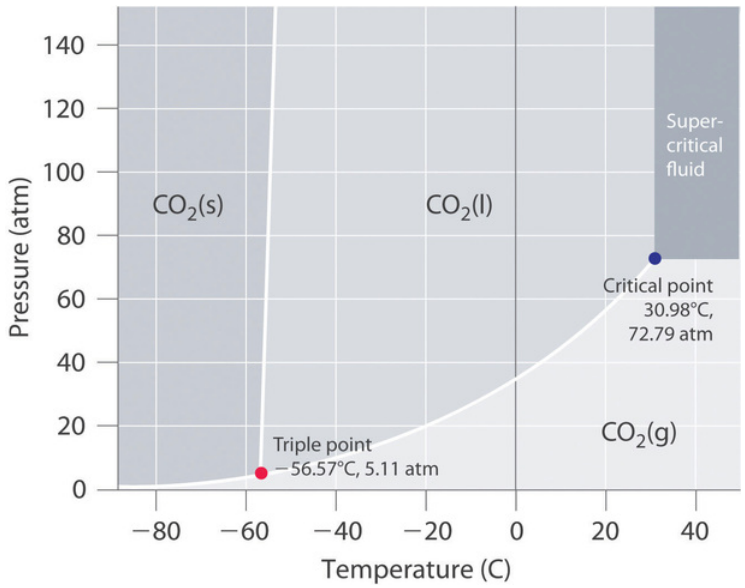


Figure **8.1.6.3**: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure **8.1.6.1**.

Figure **8.1.6.1**: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Supercritical Fluids

To understand what happens at the critical point, consider the effects of temperature and pressure on the densities of liquids and gases, respectively. As the temperature of a liquid increases, its density decreases. As the pressure of a gas increases, its density increases. At the critical point, the liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluid, which exhibits many of the properties of a gas but has a density more typical of a liquid. For example, the density of water at its critical point (T = 374°C, P = 217.7 atm) is 0.32 g/mL, about one-third that of liquid water at room temperature but much greater than that of water vapor under most conditions. The transition between a liquid/gas mixture and a supercritical phase is demonstrated for CO_2 in Figure 8.1.6.4. At the critical temperature, the meniscus separating the liquid and gas phases disappears.



Figure 8.1.6.4: Liquid CO_2 is heated in a pressure cell until it reaches the critical point were it changes into a supercritical fluid.Below the critical temperature the meniscus between the liquid and gas phases is apparent. At the critical temperature, the meniscus disappears because the density of the vapor is equal to the density of the liquid. Above T_c, a dense homogeneous fluid fills the tube.

In the last few years, supercritical fluids have evolved from laboratory curiosities to substances with important commercial applications. For example, carbon dioxide has a low critical temperature (31°C), a comparatively low critical pressure (73 atm), and low toxicity, making it easy to contain and relatively safe to manipulate. Because many substances are quite soluble in supercritical CO_2, commercial processes that use it as a solvent are now well established in the oil industry, the food industry, and others. Supercritical CO_2 is pumped into oil wells that are no longer producing much oil to dissolve the residual oil in the underground reservoirs. The less-viscous solution is then pumped to the surface, where the oil can be recovered by evaporation (and recycling) of the CO_2. In the food, flavor, and fragrance industry, supercritical CO_2 is used to extract components from natural substances for use in perfumes, remove objectionable organic acids from hops prior to making beer, and selectively extract caffeine from whole coffee beans without removing important flavor components. The latter process was patented in 1974, and now virtually all decaffeinated coffee is produced this way. The earlier method used volatile organic solvents such as methylene chloride (dichloromethane [CH_2Cl_2], boiling point = 40°C), which is difficult to remove completely from the beans and is known to cause cancer in laboratory animals at high doses.

Summary

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a **phase diagram**, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point. Within a given region, only a single phase is stable, but along the lines that separate the regions, two phases are in equilibrium at a given temperature and pressure. The lines separating the three phases intersect at a single point, the **triple point**, which is the only combination of temperature and pressure at which all three phases can coexist in equilibrium. Water has an unusual phase diagram: its melting point decreases with increasing pressure

because ice is less dense than liquid water. The phase diagram of carbon dioxide shows that liquid carbon dioxide cannot exist at atmospheric pressure. Consequently, solid carbon dioxide sublimes directly to a gas.

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8.1.7: The Born-Haber Cycle

We can measure the strength of a covalent bond, because we can usually break a covalently-bonded molecule into fragments and measure the energy required to do so. For example, if we want to measure the bond energy in HCl, we can carry out the reaction:

$\mathbf{HCl\,(g) \longrightarrow H\,(g) + Cl\,(g)}$

However, we cannot measure the strength of an ionic bond this way, because ionic compounds do not break apart into gaseous ions:

$NaCl(s) \longrightarrow Na^{+}(g) + Cl^{-}(g)$

Born-Haber cycles are used to estimate the strength of "ionic bonds" in compounds such as NaCl.

An Application of Hess's Law

In a Born-Haber cycle, we carry out the following sequence of reactions:

Elements (in their standard states)	$\longrightarrow$	Gaseous atoms	$\longrightarrow$	Gaseous ions	$\longrightarrow$	Compound

The energy of each step except the last one can be measured experimentally. In addition, we can measure the energy of the single-step reaction below (this is the "heat of formation" of the compound):

Elements (in their standard states) $\longrightarrow$ Compound

By Hess's Law, the energies of the reactions in the first sequence must add up to the heat of formation (the energy of the single-step reaction).

The basic concept is not hard. The difficult is in keeping the details straight. Ionic compounds contain two (or more) elements, each of which must be converted to gaseous atoms and then to gaseous ions. For example, here are the steps required to convert elemental calcium (a solid at room temperature) to gaseous calcium ions:

Sublime the solid calcium (convert it to a gas): $Ca(s) \longrightarrow Ca(g)$

Remove one electron from each atom: $Ca(g) \longrightarrow Ca^{+}(g) + e^{-}$

Remove a second electron from each atom: $Ca^{+}(g) \longrightarrow Ca^{2+}(g) + e^{-}$

Nonmetals often form covalent molecules. If so, you must break the covalent bond as part of this process. Here are the steps required to convert elemental bromine (a diatomic liquid at room temperature) to gaseous bromide ions:

Vaporize the liquid bromine (convert it to a gas): $Br_2(l) \longrightarrow Br_2(g)$

Break the covalent bond in Br_2: $Br_2(g) \longrightarrow 2\,Br(g)$

Add an electron to each atom: $Br(g) + e^{-} \longrightarrow Br^{-}(g)$

Your job in sorting out a Born-Haber cycle has two parts. The first is to be able to figure out exactly what reactions must occur when you convert the original element to a monatomic gas. The second is to know how to identify the energy of each reaction type.

The reaction types that you might see in a Born-Haber cycle

1) **Heat of sublimation (ΔH_{sub})**:this is the energy required to convert a solid to a gas. For metals and most solid nonmetals, sublimation produces a monatomic gas. Heats of sublimation are always positive numbers. For iodine (which is diatomic), sublimation produces $I_2(g)$.

$Na(s) \longrightarrow Na(g)$ $S(s) \longrightarrow S(g)$ $I_2(s) \longrightarrow I_2(g)$

2) **Heat of vaporization (ΔH_{vap})**: this is the energy required to convert a liquid to a gas. Heats of vaporization are always positive numbers. The only elements for which this will come into play are bromine and mercury, which are liquids at room temperature.

$Hg(l) \longrightarrow Hg(g)$ $Br_2(l) \longrightarrow Br_2(g)$

3) **Bond dissociation energy (BDE, or ΔH_{BDE})**: this is the energy required to break a covalent bond. Bond dissociation energies are always positive numbers. Bond dissociation energies only come into play for the diatomic nonmetals (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2 and At_2). In these cases, sublimation or vaporization gives us diatomic molecules, not individual atoms, so we must also break the covalent bonds in the gaseous form.

$H_2(g) \longrightarrow 2\ H(g)$ $N_2(g) \longrightarrow 2\ N(g)$

4) **Ionization energy (IE, or ΔH_{IE})**: this is the energy required to remove one electron from a gaseous atom. Since many ionic compounds contain metals that have lost two or more electrons, we often need to consider two or more successive ionization energies. For example, if we need to make aluminum ions, we must remove three electrons from Al(g), so we must consider the first three ionization energies of aluminum:

$Al(g) \longrightarrow Al^+(g) + e^-$ ΔH_{IE1} = "first ionization energy" (IE1)

$Al^+(g) \longrightarrow Al^{2+}(g) + e^-$ ΔH_{IE2} = "second ionization energy" (IE2)

$Al^{2+}(g) \longrightarrow Al^{3+}(g) + e^-$ ΔH_{IE3} = "third ionization energy" (IE3)

Ionization energies are always positive numbers, and they increase as you remove more electrons (so IE1 < IE2 < IE3 for any given element).

5) **Electron affinity (EA, or ΔH_{EA})**: this is the energy absorbed or released when you add one electron to a gaseous atom. In general, only the first electron affinity can be measured directly, because negative ions repel electrons. However, the second (and third, if necessary) electron affinity can be estimated using a variation on the Born-Haber cycle. Here are the reactions that must be considered if you need to make oxide ions.

$O(g) + e^- \longrightarrow O^-(g)$ ΔH_{EA1} = "first electron affinity" (EA1, or simply EA)

$O^-(g) + e^- \longrightarrow O^{2-}(g)$ ΔH_{EA2} = "second electron affinity" (EA2)

The first electron affinity is usually a negative number (a few elements have positive EA's). The second EA (and beyond) is always positive.

6) **Solution energy (ΔH_{soln})**: this is the energy released or absorbed for the solution process of an ionic compound. Here is the reaction that must be considered for the solution of $AlF_3(s)$.

$AlF_3(s) \longrightarrow Al^{3+}(aq) + 3\ F^-(aq)$

7) **Hydration energy (HE, or ΔH_{HE})**: this is the energy released for the solution of gaseous ions of a compound. The hydration energy is a measure of all the ion-dipole attractions between the ions on the water solvent. Here is the reaction that must be considered for the hydration of the ions of $AlF_3(s)$.

$Al^{3+}(g) + 3\ F^-(g) \longrightarrow Al^{3+}(aq) + 3\ F^-(aq)$

8) **Crystal lattice energy (CLE, or ΔH_{CLE})**: this is the energy released when gaseous ions are converted into the solid ionic compound. For example, the lattice energy of aluminum fluoride corresponds to the following reaction:

$Al^{3+}(g) + 3\ F^-(g) \longrightarrow AlF_3(s)$

Lattice energies are always large negative numbers, ranging from around –600 to –13,000 kJ/mol.

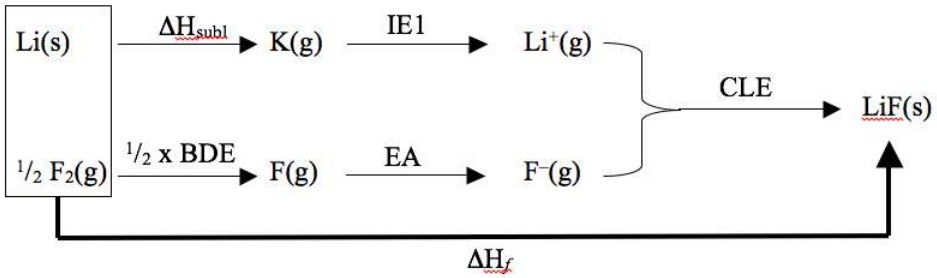
9) **Heat of formation (ΔH_f)**: this is the energy absorbed or released when you make an ionic compound from its constituent elements (as they normally appear at room temperature and 1 atm pressure). For aluminum fluoride, the corresponding reaction is:

$Al(s) + {}^3/_2\ F_2(g) \longrightarrow AlF_3(s)$

Heats of formation are virtually always negative numbers for ionic compounds.

Putting the reactions together:

Here is an example of how these reactions can be fitted together to make the complete Born-Haber cycle for LiF. We start with solid Li and gaseous F_2, the standard states of these elements at room temperature and 1 atm pressure.



Energy "bookkeeping": ΔH_{sub} + **IE1** + $^1/_2$·**BDE** + **EA** + **CLE** = ΔH_f

For CaI_2, the energy bookkeeping would look like this (see if you can figure out why). Note that there are two heats of sublimation involved, because both calcium and iodine are solids at room temperature.

ΔH_{sub}(Ca) + **IE1** + **IE2** + **BDE** + ΔH_{sub}(I_2) + 2·**EA** + **CLE** = ΔH_f

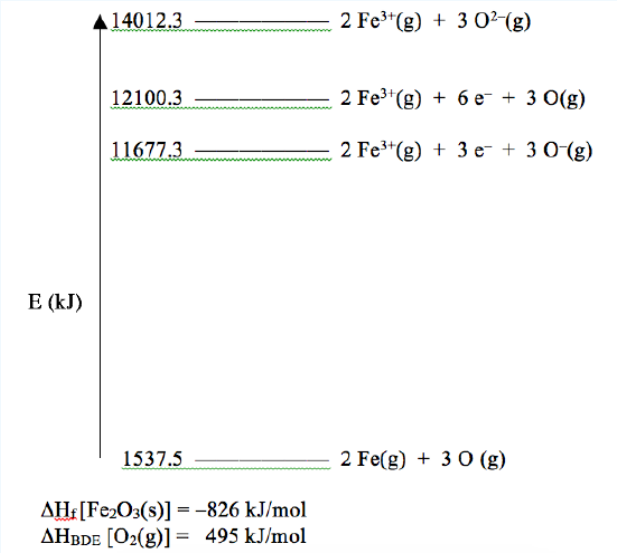
For Al_2O_3, the energy bookkeeping would look like this. Again, see if you can figure out why. Note that in this case, we must include two electron affinities for oxygen, because the charge on oxygen is –2 in this compound.

$2\cdot\Delta H_{sub}$ + 2·**IE1** + 2·**IE2** + 2·**IE3** + $^3/_2$·**BDE** + 3·**EA1** + 3·**EA2** + **CLE** = ΔH_f

These problems can also be approached in terms of an energy diagram (as shown in the following example problem).

Example 8.1.7.1

Given the partial Born-Haber energy level diagram below, along with the ΔH values provided, answer the questions that follow.



a. Determine $\Delta H_{sublimation}$ [Fe]

b. Determine ΔH_{CLE} [Fe_2O_3]

c. Determine ΔH_{EA1} [O(g)]

d. Determine ΔH_{EA2} [O(g)]

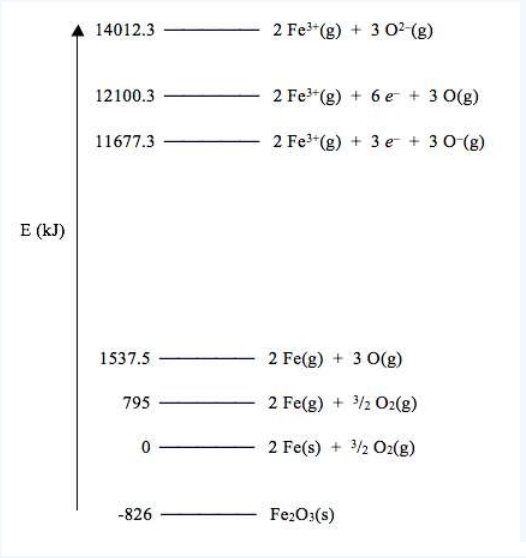
e. What is the value for the sum (ΔH_{IE1} [Fe(g)] + ΔH_{IE2} [Fe(g)] + ΔH_{IE3} [Fe(g)])?

Solution

To solve this problem, we can begin by using the energies given below the diagram to draw a couple of additional energy levels….

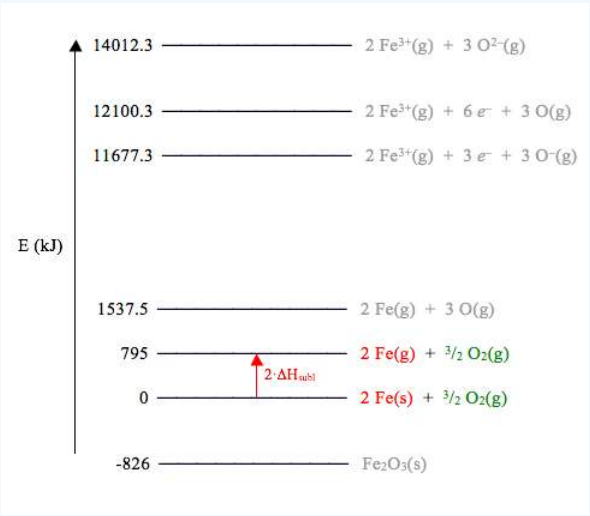
- In any Born-Haber diagram, the energy of the elements in their standard states (Fe(s) + $^3/_2$ O_2(g) in this case) is zero.
- The ΔH_f of Fe_2O_3(s) is -826 kJ/mol, so the energy of Fe_2O_3(s) is -826 kJ.
- The bond dissociation energy of O_2(g) is 495 kJ/mol, so converting $^3/_2$ of a mole of O_2(g) into 3 moles of O(g) requires $^3/_2$(495 kJ) = 742.5 kJ. On the diagram in the problem, the lowest level that contains 3 O(g) is the one at the bottom (labeled 2 Fe(g) + 3 O(g)). Therefore, the level corresponding to 2 Fe(g) + $^3/_2$ O_2(g) must be 742.5 kJ below this. 1537.5 kJ – 742.5 kJ = 795 kJ.

Below, we've redrawn the Born-Haber diagram with these additional energy values.

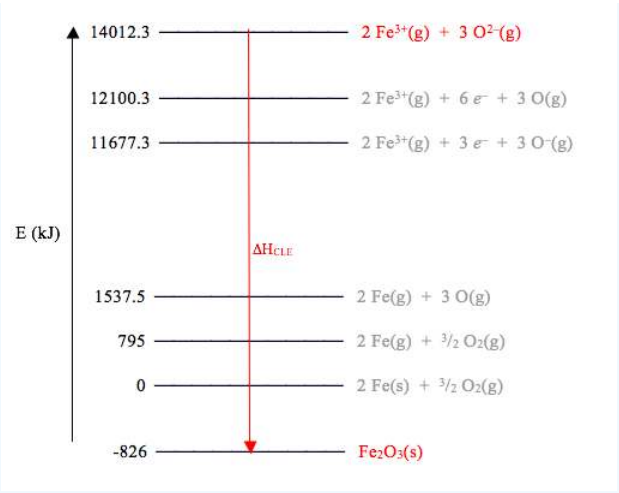


Now we can use this diagram to answer the questions. For each question, the following diagram shows the relevant ΔH value. The substances that change are shown in red, and substances that are spectators during the reaction are shown in green.

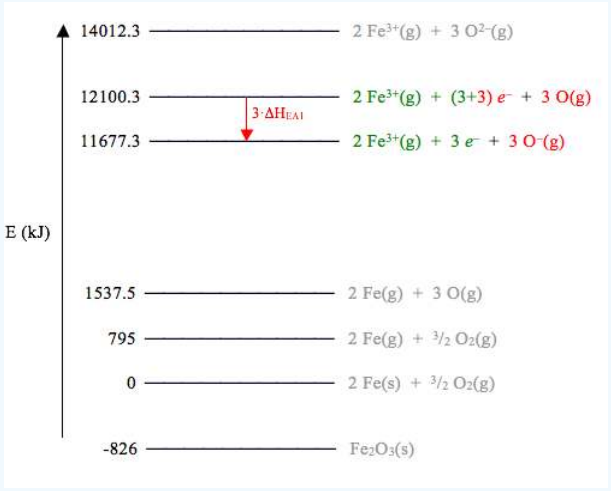
a) Comparing the levels at E = 0 and E = 795 kJ, we see that the only change is 2 Fe(s) -> 2 Fe(g). This is the reaction for the sublimation of Fe(s). Therefore, ΔH = 795 kJ – 0 kJ = 795 kJ for this reaction. Since this energy corresponds to the sublimation of 2 moles of Fe, the enthalpy of sublimation is 795 kJ/2 mol = **397.5 kJ/mol**.



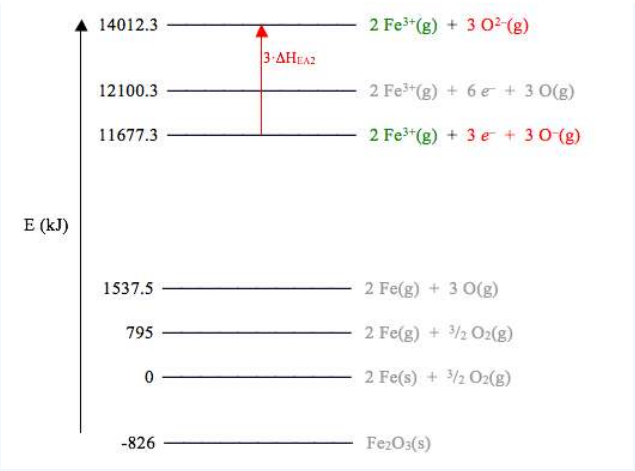
b) The crystal lattice energy is the energy change on going from the gaseous ions to the solid compound: 2 Fe^{3+}(g) + 3 O^{2-}(g) -> Fe_2O_3(s). From the diagram, we can calculate this energy change: ΔH = (-826 kJ) – 14012.3 kJ = -14838.3 kJ. Since this corresponds to the formation of one mole of Fe_2O_3, the crystal lattice energy is **-14838.3 kJ/mol.**



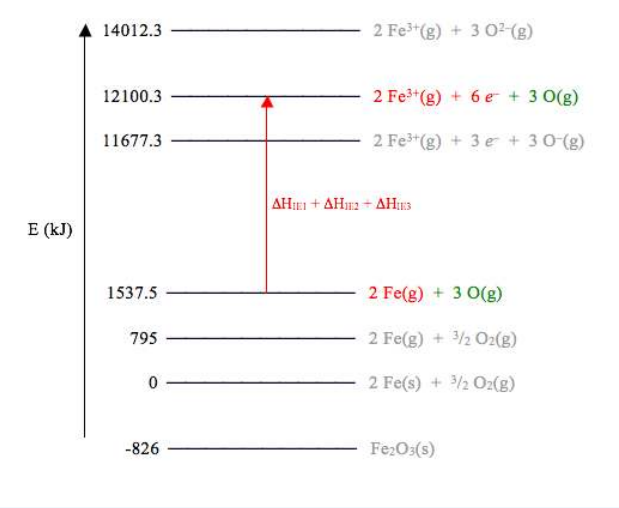
c) EA1 for oxygen is the energy change for the reaction O(g) -> O^-(g). Looking at the diagram, we see that going from the 12100.3 kJ level to the 11677.3 kJ level corresponds to the reaction 3 O(g) -> 3 O^-(g), which is the right reaction, just multiplied by 3. (The iron remains in the same state, so it is a spectator here. Therefore, ΔH = 11677.3 kJ – 12100.3 kJ = -423 kJ for this reaction. Since this energy corresponds to the ionization of three moles of O, the EA1 is -423 kJ/3 mol = **-141 kJ/mol.**



d) EA2 for oxygen is the energy change for the reaction O^-(g) -> O^{2-}(g). Looking at the diagram, we see that going from the 11677.3 kJ level to the 14012.3 kJ level corresponds to the reaction 3 O^-(g) -> 3 O^{2-}(g), which is the right reaction, just multiplied by 3. (Again, the iron remains in the same state.) Therefore, ΔH = 14012.3 kJ - 11677.3 kJ = 2335 kJ for this reaction. Since this energy corresponds to the ionization of three moles of O, the EA2 is 2335 kJ/3 mol = **778.3 kJ/mol.**



e) The sum of the three IE's for iron is the total energy required to convert a mole of Fe(g) into a mole of $Fe^{3+}(g)$, corresponding to the reaction Fe(g) ® $Fe^{3+}(g)$ + 3 e^-. Looking at the diagram, we see that going from the 1537.5 kJ level to the 12100.3 kJ level corresponds to the reaction 2 Fe(g) ® 2 $Fe^{3+}(g)$ + 6 e^-, which is the right reaction, just multiplied by 2. Note that we had to go to the 12100.3 kJ level in order to keep the oxygen in the same state, 3 O(g). Therefore, ΔH = 12100.3 kJ – 1537.5 kJ = 10562.8 kJ for this reaction. Since this energy corresponds to the ionization of two moles of Fe, the correct answer is 10562.8 kJ/2 mol = **5281.4 kJ/mol.**



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