CHM 120: SURVEY OF GENERAL CHEMISTRY



Jesse Crandall
Grand Rapids Community College

LibreTexts™

CHM 120: Survey of General Chemistry

Jesse Crandall

Grand Rapids Community College

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide an accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden born from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by NICE CXone Expert and was supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org or visit our main website at https://LibreTexts.org.

This text was compiled on 04/29/2026

TABLE OF CONTENTS

Licensing

1: Introduction to Chemistry

- 1.1: Introduction
- 1.2: Phases and Classification of Matter
- 1.3: Physical and Chemical Properties
- 1.4: Exercises
  - 1.4.1: Answers to Selected Exercises

2: Measurements and the Periodic Table

- 2.1: Measurements
- 2.2: Measurement Uncertainty, Accuracy, and Precision
- 2.3: Mathematical Treatment of Measurement Results
- 2.4: The Periodic Table
- 2.5: Chemical Formulas
- 2.6: Atomic Structure and Symbolism
  - 2.6.1: Extra-Early Atomic Theory
  - 2.6.2: Extra-Evolution of Atomic Theory
- 2.7: Radioactive Decay
  - 2.7.1: Nuclear Equations
  - 2.7.2: Extra-Uses of Radioisotopes
  - 2.7.3: Extra-Biological Effects of Radiation
- 2.8: Exercises
  - 2.8.1: Answers to Selected Exercises
- 2.9: Exercises for Nuclear Reactions
  - 2.9.1: Answers to Exercises for Nuclear Reactions

3: Ions, Compounds, and Molecules

- 3.1: Molecular and Ionic Compounds
- 3.2: Chemical Nomenclature
- 3.3: Electronic Structure of Atoms (Electron Configurations)
  - 3.3.1: Extra-Orbital Origin and Shape
- 3.4: Ionic Bonding
- 3.5: Covalent Bonding
- 3.6: Exercises
  - 3.6.1: Answers to Selected Exercises

4: Lewis Structures; Geometry and Polarity of Molecules

- 4.1: Lewis Symbols and Structures
  - 4.1.1: Extra-Formal Charges and Resonance
- 4.2: Molecular Structure and Polarity
- 4.3: Hybrid Atomic Orbitals

- 4.3.1: Extra-Multiple Bonds
- 4.4: Intermolecular Forces
  - 4.4.1: Extra-Properties of Liquids
- 4.5: Exercises (Lewis Structures)
  - 4.5.1: Answers to Selected Exercises
- 4.6: Exercises (Intermolecular Forces)
  - 4.6.1: Answers to Selected Exercises

5: Moles, Molar Mass, Concentration, and Solutions

- 5.1: Formula Mass and the Mole Concept
- 5.2: Determining Empirical and Molecular Formulas
- 5.3: Molarity
- 5.4: The Dissolution Process
- 5.5: Electrolytes
- 5.6: Exercises (Solutions and Concentrations)
  - 5.6.1: Answers to Selected Exercises
- 5.7: Exercises (Moles and Chemical Formulas)
  - 5.7.1: Answers to Selected Exercises (Moles and Chemical Formulas)

6: Gases and the Ideal Gas Law

- 6.1: Gas Pressure
- 6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
  - 6.2.1: Molar Mass of a Gas and Dalton's Law
  - 6.2.2: The Kinetic-Molecular Theory
- 6.3: Exercises
  - 6.3.1: Answers to Selected Exercises

7: Chemical Reactions and Stoichiometry

- 7.1: Writing and Balancing Chemical Equations
- 7.2: Classifying Chemical Reactions
- 7.3: Reaction Stoichiometry
- 7.4: Reaction Yields
- 7.5: Exercises
  - 7.5.1: Answers to Selected Exercises

8: Kinetics- Rates of Chemical Reactions

- 8.1: Chemical Reaction Rates
- 8.2: Factors Affecting Reaction Rates
- 8.3: Rate Laws
- 8.4: Catalysis
- 8.5: Exercises
  - 8.5.1: Answers to selected Exercises

9: Equilibrium and Acid Base Chemistry

- 9.1: Chemical Equilibria
- 9.2: Equilibrium Constants
- 9.3: Shifting Equilibria- Le Châtelier's Principle
- 9.4: Brønsted-Lowry Acids and Bases
  - 9.4.1: Buffers
  - 9.4.2: Acid-Base Titrations
- 9.5: pH and pOH
- 9.6: Exercises (Equilibrium)
  - 9.6.1: Chapter 13
- 9.7: Exercises (Acid-Base)
  - 9.7.1: Answers to Selected Exercises

10: Thermochemistry and Thermodynamics

- 10.1: Energy Basics
- 10.2: Calorimetry
- 10.3: Enthalpy
- 10.4: Thermodynamics
  - 10.4.1: Spontaneity
    - 10.4.1.1: Entropy
    - 10.4.1.2: The Second and Third Laws of Thermodynamics
  - 10.4.2: New Page
- 10.5: Free Energy
- 10.6: Exercises (Thermochemistry)
  - 10.6.1: Answers to Selected Exercises
- 10.7: Exercises (Thermodynamics)
  - 10.7.1: Answers to Selected Exercises

Appendix: Standard Thermodynamic Properties for Selected Substances

Index

Glossary

Detailed Licensing

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Introduction to Chemistry

1.1: Introduction
1.2: Phases and Classification of Matter
1.3: Physical and Chemical Properties
1.4: Exercises
1.4.1: Answers to Selected Exercises

This page titled 1: Introduction to Chemistry is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

1.1: Introduction

Your alarm goes off and, after hitting “snooze” once or twice, you pry yourself out of bed. You make a cup of coffee to help you get going, and then you shower, get dressed, eat breakfast, and check your phone for messages. On your way to school, you stop to fill your car’s gas tank, almost making you late for the first day of chemistry class. As you find a seat in the classroom, you read the question projected on the screen: “Welcome to class! Why should we study chemistry?”



Figure **1.1.1**: Chemical substances and processes are essential for our existence, providing sustenance, keeping us clean and healthy, fabricating electronic devices, enabling transportation, and much more. (credit “left”: modification of work by “vxla”/Flickr; credit “left middle”: modification of work by “the Italian voice”/Flickr; credit “right middle”: modification of work by Jason Trim; credit “right”: modification of work by “gosheshe”/Flickr)

Do you have an answer? You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. 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.

This page titled 1.1: Introduction is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

- **1.0: Introduction** is licensed CC BY 4.0.

1.2: Phases and Classification of Matter

Learning Objectives

By the end of this section, you will be able to:

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

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 not inflate (increase its volume) when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure **1.2.1**). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of its 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.

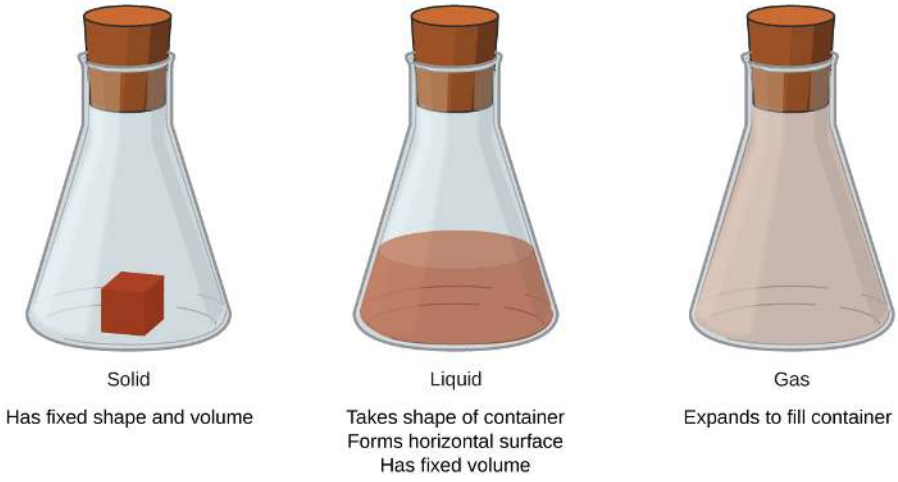


Figure **1.2.1**: The three most common states or phases of matter are solid, liquid, and gas.

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 **1.2.2**). 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 1.2.2: A plasma torch can be used to cut metal. (credit: “Hypertherm”/Wikimedia Commons)

Link to Learning

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 1.2.3). 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.

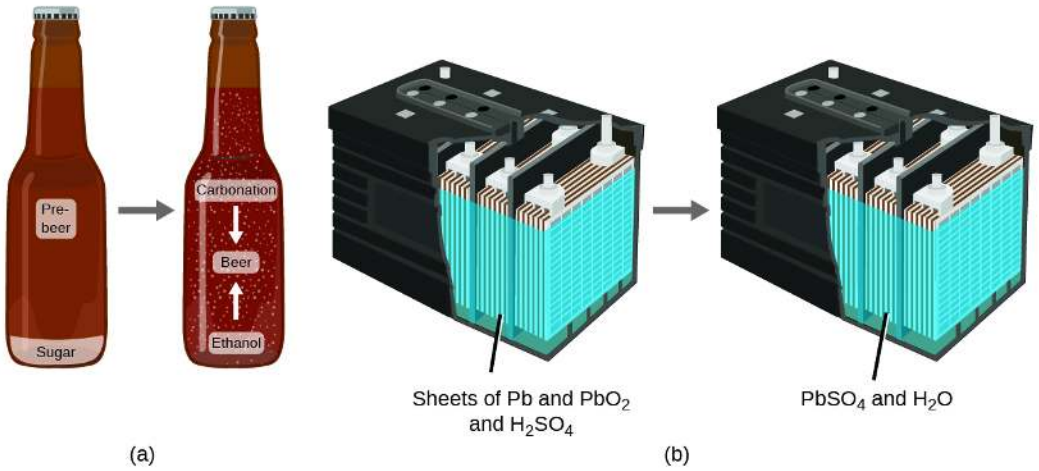


Figure **1.2.3**: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbon dioxide. (b) The mass of the lead, lead oxide, and sulfuric acid consumed by the production of electricity is exactly equal to the mass of lead sulfate and water that 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.

1.2.1: Classifying Matter

Matter can be classified 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.

Pure substances may be divided 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 are comprised of two or more elements are called compounds. Compounds may be broken down by chemical changes to yield 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 **1.2.4**). 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).

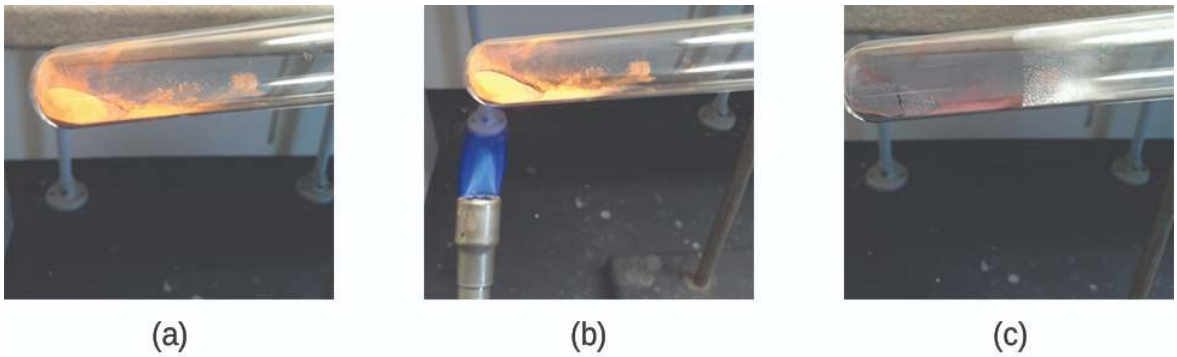


Figure **1.2.4**: (a) The compound mercury(II) oxide, (b) when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

Link to Learning

Many compounds break down when heated. This site shows the breakdown of mercury oxide, HgO. You can also view an example of the photochemical decomposition of silver chloride (AgCl), the basis of early photography.

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 **1.2.5**). Its composition can vary because it may be prepared 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 **1.2.5**). 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 **1.2.5**: (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 that 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 **1.2.6**).

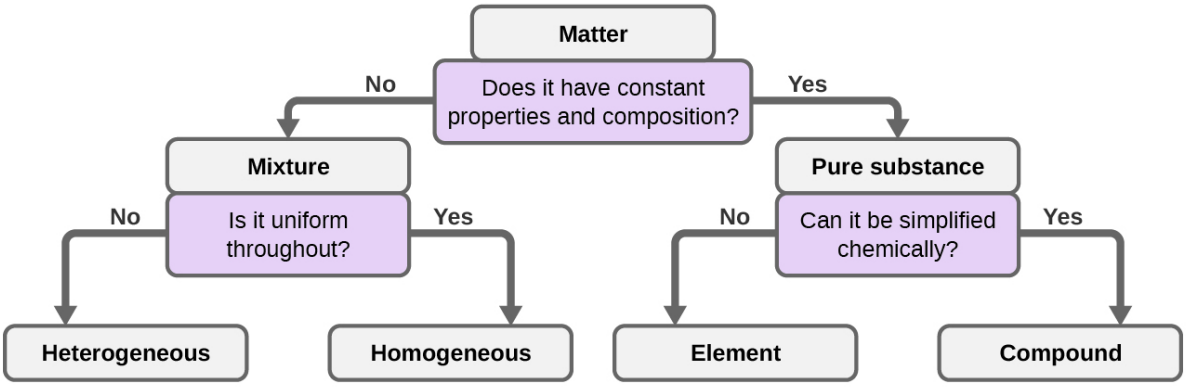


Figure **1.2.6**: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere (Table **1.2.1**). 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 **1.2.1**: 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

1.2.2: 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 **1.2.7**). This atom would no longer be gold if it were divided any further.

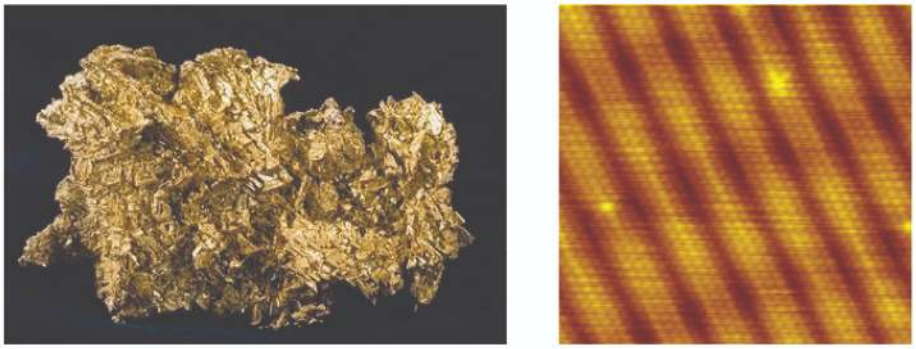


Figure **1.2.7**: (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: 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 **1.2.8**) shows increasingly close microscopic and atomic-level views of ordinary cotton.

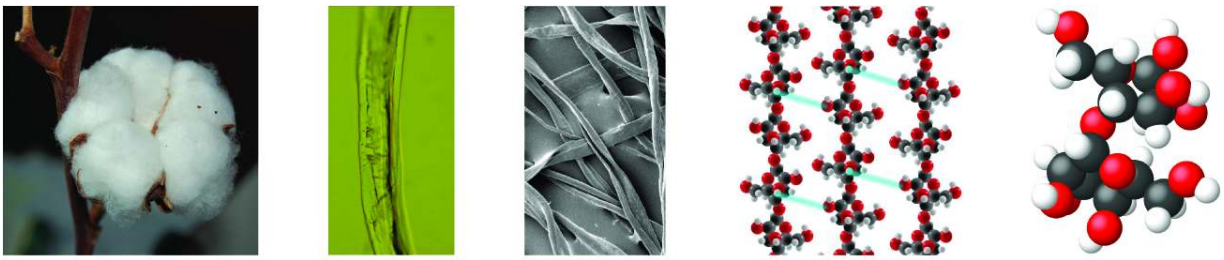


Figure **1.2.8**: These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (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 **1.2.9**). 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.

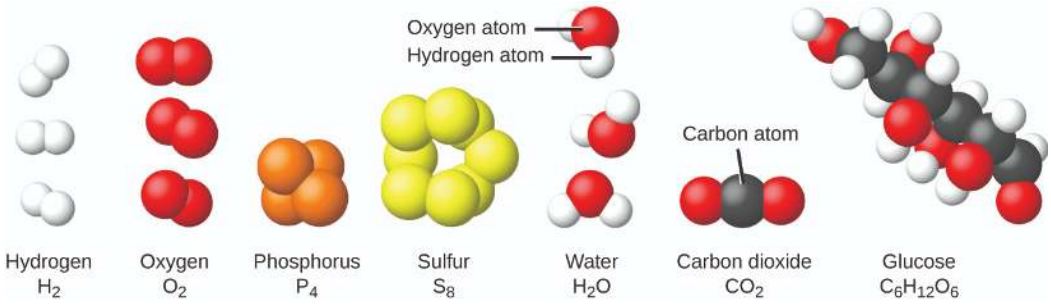


Figure **1.2.9**: The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

Chemistry in Everyday Life: 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 **1.2.10**).

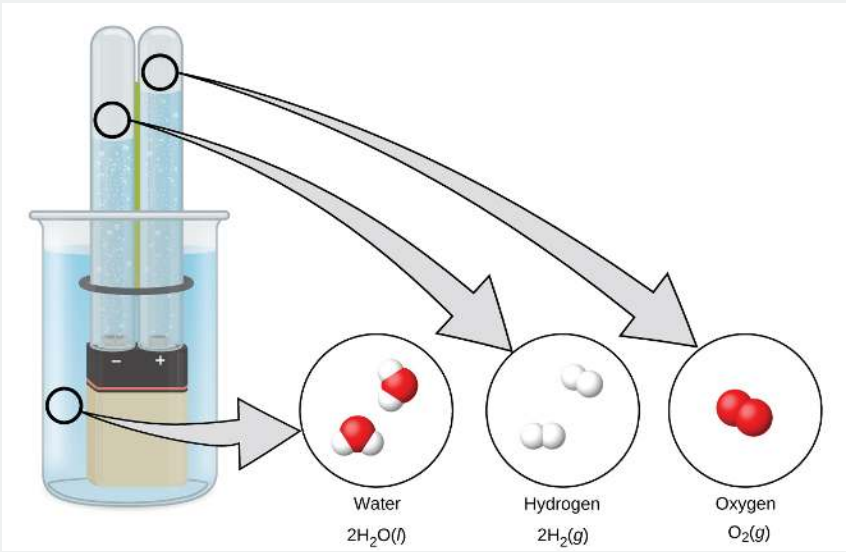


Figure **1.2.10**: The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, 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, 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 **1.2.11**). 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.

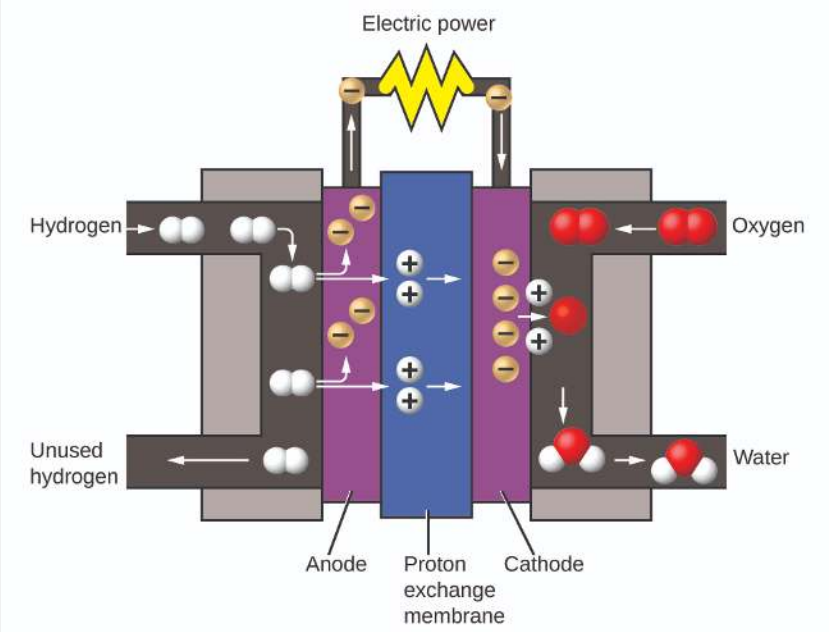


Figure 1.2.11: A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

Chemistry in Everyday Life: Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 1.2.12) 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 composed 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.

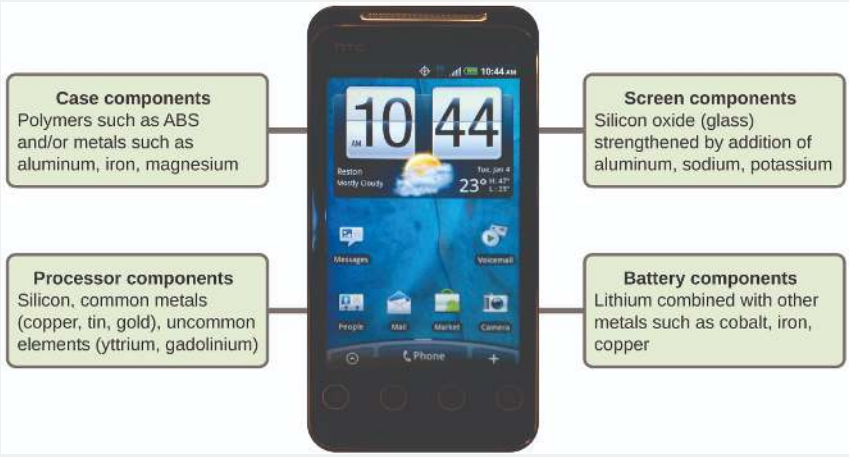


Figure 1.2.12: Almost one-third of naturally occurring elements are used to make a cell phone. (credit: modification of work by John Taylor)

This page titled 1.2: Phases and Classification of Matter is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **1.2: Phases and Classification of Matter** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.3: Physical and Chemical Properties

Learning Objectives

By the end of this section, you will be able to:

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

The characteristics that 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. Some physical properties, such as density and color, may be observed without changing the physical state of the matter. 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 the chemical identities of the substances contained in the matter. Physical changes are observed when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure **1.3.1**). 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.



(a) (b)

Figure **1.3.1**: (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, and many other types of reactivity. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure **1.3.2**). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.



(a) (b)

Figure **1.3.2**: (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)

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 **1.3.3**).

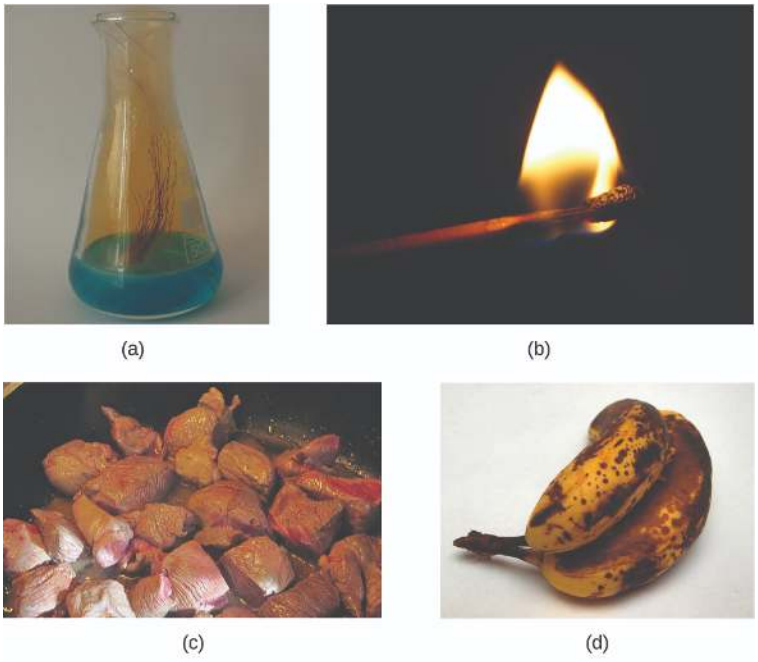


Figure **1.3.3**: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat 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 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).

Chemistry in Everyday Life: Hazard Diamond

You may have seen the symbol shown in Figure **1.3.4**: 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.

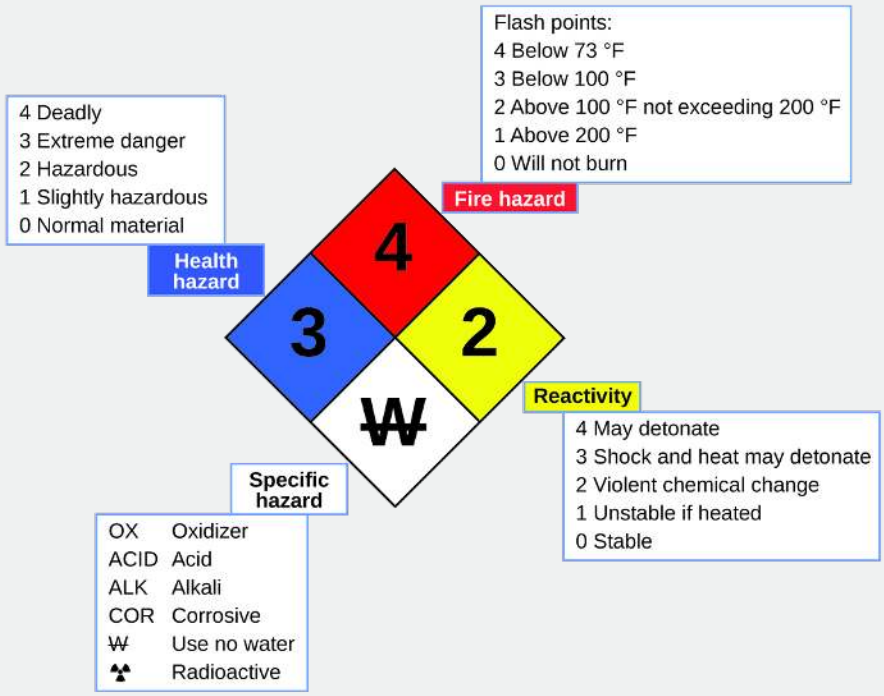


Figure **1.3.4**: The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

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. 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 intermediate conductivities).

The periodic table is a table of elements that places elements with similar properties close together (Figure **1.3.5**). You will learn more about the periodic table as you continue your study of chemistry.

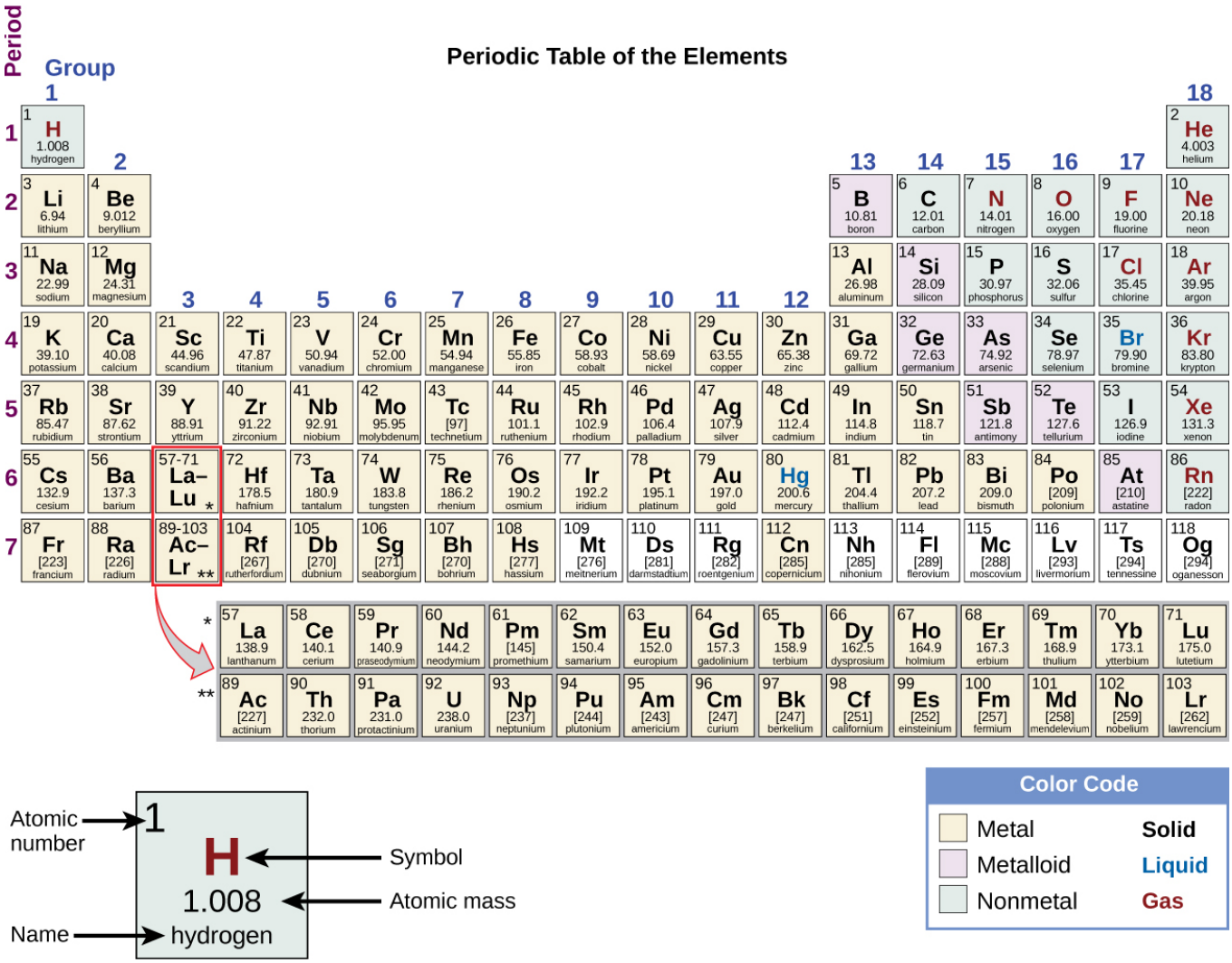


Figure **1.3.5**: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

This page titled 1.3: Physical and Chemical Properties is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **1.3: Physical and Chemical Properties** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.4: Exercises

1. Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.

2. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

a. Falling barometric pressure precedes the onset of bad weather.
b. All life on earth has evolved from a common, primitive organism through the process of natural selection.
c. My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

3. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

a. The pressure of a sample of gas is directly proportional to the temperature of the gas.
b. Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
c. At a higher temperature, solids (such as salt or sugar) will dissolve better in water.

4. Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

a. The mass of a lead pipe is 14 lb.
b. The mass of a certain chlorine atom is 35 amu.
c. A bottle with a label that reads Al contains aluminum metal.
d. Al is the symbol for an aluminum atom.

5. Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

a. A certain molecule contains one H atom and one Cl atom.
b. Copper wire has a density of about 8 g/cm^3.
c. The bottle contains 15 grams of Ni powder.
d. A sulfur molecule is composed of eight sulfur atoms.

6. According to one theory, the pressure of a gas increases as its volume decreases because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behavior? Explain your answer.

7. The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

8. Why is an object's mass, rather than its weight, used to indicate the amount of matter it contains?

9. What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

10. How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

11. How does a homogeneous mixture differ from a pure substance? How are they similar?

12. How does an element differ from a compound? How are they similar?

13.

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

14. How does an atom differ from a molecule? In what ways are they similar?

15. Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.

16. Classify each of the following as an element, a compound, or a mixture:

a. copper

b. water
c. nitrogen
d. sulfur
e. air
f. sucrose
g. a substance composed of molecules each of which contains two iodine atoms
h. gasoline

17. Classify each of the following as an element, a compound, or a mixture:

a. iron
b. oxygen
c. mercury oxide
d. pancake syrup
e. carbon dioxide
f. a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom
g. baking soda
h. baking powder

18. A sulfur atom and a sulfur molecule are not identical. What is the difference?

19. How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

20. Why are astronauts in space said to be “weightless,” but not “massless”?

21. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

22. Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.

23. When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide called rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?

24. As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:

a. Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.
b. When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.
c. Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

25. Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

a. If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?
b. If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.
c. If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

26. Classify the six underlined properties in the following paragraph as chemical or physical:

Fluorine is a pale yellow gas that reacts with most substances. The free element melts at −220 °C and boils at −188 °C. Finely divided metals burn in fluorine with a bright flame. Nineteen grams of fluorine will react with 1.0 gram of hydrogen.

27. Classify each of the following changes as physical or chemical:

a. condensation of steam
b. burning of gasoline
c. souring of milk
d. dissolving of sugar in water
e. melting of gold

28. Classify each of the following changes as physical or chemical:

a. coal burning
b. ice melting
c. mixing chocolate syrup with milk
d. explosion of a firecracker
e. magnetizing of a screwdriver

29. The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?

30. A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?

31. Explain the difference between extensive properties and intensive properties.

32. Identify the following properties as either extensive or intensive.

a. volume
b. temperature
c. humidity
d. heat
e. boiling point

33. The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its volume (V).

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

34. Is one liter about an ounce, a pint, a quart, or a gallon?

35. Is a meter about an inch, a foot, a yard, or a mile?

36. Indicate the SI base units or derived units that are appropriate for the following measurements:

a. the length of a marathon race (26 miles 385 yards)
b. the mass of an automobile
c. the volume of a swimming pool
d. the speed of an airplane
e. the density of gold
f. the area of a football field
g. the maximum temperature at the South Pole on April 1, 1913

37. Indicate the SI base units or derived units that are appropriate for the following measurements:

a. the mass of the moon
b. the distance from Dallas to Oklahoma City
c. the speed of sound
d. the density of air

e. the temperature at which alcohol boils
f. the area of the state of Delaware
g. the volume of a flu shot or a measles vaccination

38. Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

a. 10^3
b. 10^{-2}
c. 0.1
d. 10^{-3}
e. $1,000,000$
f. 0.000001

39. Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

a. c
b. d
c. G
d. k
e. m
f. n
g. p
h. T

40. A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

a. Determine the density of this piece of jewelry.
b. Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

41. Visit this density simulation and click the "turn fluid into water" button to adjust the density of liquid in the beaker to 1.00 g/mL.

a. Use the water displacement approach to measure the mass and volume of the unknown material (select the green block with question marks).
b. Use the measured mass and volume data from step (a) to calculate the density of the unknown material.
c. Assuming this material is a copper-containing gemstone, identify its three most likely identities by comparing the measured density to the values tabulated at this gemstone density guide.
d. How are mass and density related for blocks of the same volume?

42. Visit this density simulation and click the "reset" button to ensure all simulator parameters are at their default values.

a. Use the water displacement approach to measure the mass and volume of the red block.
b. Use the measured mass and volume data from step (a) to calculate the density of the red block.
c. Use the vertical green slide control to adjust the fluid density to values well above, then well below, and finally nearly equal to the density of the red block, reporting your observations.

43. Visit this density simulation and click the “turn fluid into water” button to adjust the density of liquid in the beaker to 1.00 g/mL. Change the block material to foam, and then wait patiently until the foam block stops bobbing up and down in the water.

a. The foam block should be floating on the surface of the water (that is, only partially submerged). What is the volume of water displaced?
b. Use the water volume from part (a) and the density of water (1.00 g/mL) to calculate the mass of water displaced.
c. Remove and weigh the foam block. How does the block’s mass compare to the mass of displaced water from part (b)?

44. Express each of the following numbers in scientific notation with correct significant figures:

a. 711.0
b. 0.239

c. 90743
d. 134.2
e. 0.05499
f. 10000.0
g. 0.000000738592

45. Express each of the following numbers in exponential notation with correct significant figures:

a. 704
b. 0.03344
c. 547.9
d. 22086
e. 1000.00
f. 0.0000000651
g. 0.007157

46. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

a. the number of eggs in a basket
b. the mass of a dozen eggs
c. the number of gallons of gasoline necessary to fill an automobile gas tank
d. the number of cm in 2 m
e. the mass of a textbook
f. the time required to drive from San Francisco to Kansas City at an average speed of 53mi/h

47. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

a. the number of seconds in an hour
b. the number of pages in this book
c. the number of grams in your weight
d. the number of grams in 3 kilograms
e. the volume of water you drink in one day
f. the distance from San Francisco to Kansas City

48 How many significant figures are contained in each of the following measurements?

a. 38.7 g
b. $2 \times 10^{18}\ \text{m}$
c. $3,486,002\ \text{kg}$
d. $9.74150 \times 10^{-4}\ \text{J}$
e. $0.0613\ \text{cm}^3$
f. 17.0 kg
g. $0.01400\ \text{g/mL}$

49. How many significant figures are contained in each of the following measurements?

a. 53 cm
b. $2.05 \times 10^{8}\ \text{m}$
c. $86,002\ \text{J}$
d. $9.740 \times 10^{4}\ \text{m/s}$
e. $10.0613\ \text{m}^3$
f. $0.17\ \text{g/mL}$
g. 0.88400 s

50. The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.

a. 0.0055 g active ingredients
b. 12 tablets
c. 3% hydrogen peroxide
d. 5.5 ounces
e. 473 mL
f. 1.75% bismuth
g. 0.001% phosphoric acid
h. 99.80% inert ingredients

51. Round off each of the following numbers to two significant figures:

a. 0.436
b. 9.000
c. 27.2
d. 135
e. 1.497×10^{-3}
f. 0.445

52. Round off each of the following numbers to two significant figures:

a. 517
b. 86.3
c. 6.382×10^{3}
d. 5.0008
e. 22.497
f. 0.885

53. Perform the following calculations and report each answer with the correct number of significant figures.

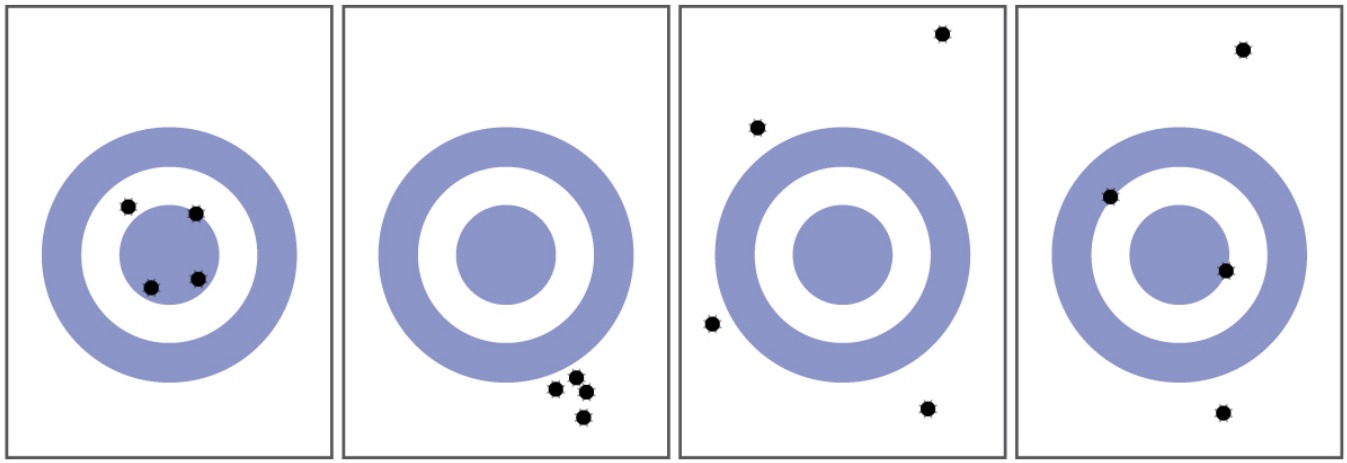
a. 628×342
b. $(5.63 \times 10^{2}) \times (7.4 \times 10^{3})$
c. $\dfrac{28.0}{13.483}$
d. 8119×0.000023
e. $14.98 + 27,340 + 84.7593$
f. $42.7 + 0.259$

54. Perform the following calculations and report each answer with the correct number of significant figures.

a. 62.8 34
b. 0.147 + 0.0066 + 0.012
c. 38 95 1.792
d. 15 – 0.15 – 0.6155
e. $8.78 \times \left(\dfrac{0.0500}{0.478}\right)$
f. 140 + 7.68 + 0.014
g. 28.7 – 0.0483
h. $\dfrac{(88.5 - 87.57)}{45.13}$

55. Consider the results of the archery contest shown in this figure.

a. Which archer is most precise?
b. Which archer is most accurate?
c. Who is both least precise and least accurate?



56. Classify the following sets of measurements as accurate, precise, both, or neither.

a. Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g
b. Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL
c. Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%

57. Write conversion factors (as ratios) for the number of:

a. yards in 1 meter
b. liters in 1 liquid quart
c. pounds in 1 kilogram

58. Write conversion factors (as ratios) for the number of:

a. kilometers in 1 mile
b. liters in 1 cubic foot
c. grams in 1 ounce

59. The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

60. The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

61. Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

62. A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimeters and grams?

63. How many milliliters of a soft drink are contained in a 12.0-oz can?

64. A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?

65. The diameter of a red blood cell is about $3\ 10^{-4}$ in. What is its diameter in centimeters?

66. The distance between the centers of the two oxygen atoms in an oxygen molecule is $1.21\ 10^{-8}$ cm. What is this distance in inches?

67. Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?

68. A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?

69. Many medical laboratory tests are run using 5.0 μL blood serum. What is this volume in milliliters?

70. If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?

71. Use scientific (exponential) notation to express the following quantities in terms of the SI base units in Table 1.2:

a. 0.13 g
b. 232 Gg
c. 5.23 pm
d. 86.3 mg
e. 37.6 cm
f. 54μ m
g. 1 Ts
h. 27 ps
i. 0.15 mK

72. Complete the following conversions between SI units.

a. 612 g = mg
b. 8.160 m = cm
c. 3779μ g = g
d. 781 mL = L
e. 4.18 kg = g
f. 27.8 m = km
g. 0.13 mL = L
h. 1738 km = m
i. 1.9Gg = g

73. Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?

74. Milk is sold by the liter in many countries. What is the volume of exactly 1/2 gal of milk in liters?

75. A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

76. Make the conversion indicated in each of the following:

a. the men's world record long jump, 29ft41/4 in., to meters
b. the greatest depth of the ocean, about 6.5 mi , to kilometers
c. the area of the state of Oregon, $96,981 mi^2$, to square kilometers
d. the volume of 1 gill (exactly 4 oz) to milliliters
e. the estimated volume of the oceans, $330,000,000 mi^3$, to cubic kilometers.
f. the mass of a 3525 − lb car to kilograms
g. the mass of a 2.3-oz egg to grams

77. Make the conversion indicated in each of the following:

a. the length of a soccer field, 120 m (three significant figures), to feet
b. the height of Mt. Kilimanjaro, at 19,565 ft, the highest mountain in Africa, to kilometers
c. the area of an 8.5 − ×11-inch sheet of paper in cm^2
d. the displacement volume of an automobile engine, $161 in^3$, to liters
e. the estimated mass of the atmosphere, 5.6×10^{15} tons, to kilograms
f. the mass of a bushel of rye, 32.0 lb , to kilograms
g. the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229oz)

78. Many chemistry conferences have held a 50-Trillion Angstrom Run (two significant figures). How long is this run in kilometers and in miles? (1 Å = 1 10^{-10} m)

79. A chemist's 50-Trillion Angstrom Run (see Exercise 1.78) would be an archeologist's 10,900 cubit run. How long is one cubit in meters and in feet? (1 Å = 1 10^{-8} cm)

80. The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms and pounds of the fuel in a full tank.

81. As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

82. To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?

83. A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

84. In a recent Grand Prix, the winner completed the race with an average speed of 229.8 km/h. What was his speed in miles per hour, meters per second, and feet per second?

85. Solve these problems about lumber dimensions.

To describe to a European how houses are constructed in the US, the dimensions of "two-by-four" lumber must be converted into metric units. The thickness width length dimensions are 1.50 in. 3.50 in. 8.00 ft in the US.

a. What are the dimensions in cm cm m?
b. This lumber can be used as vertical studs, which are typically placed 16.0 in. apart. What is that distance in centimeters?

86. The mercury content of a stream was believed to be above the minimum considered safe—1 part per billion (ppb) by weight. An analysis indicated that the concentration was 0.68 parts per billion. What quantity of mercury in grams was present in 15.0 L of the water, the density of which is 0.998 g/ml?

87. Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.

88. Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm^3?

89. Calculate these masses.

a. What is the mass of 6.00 cm^3 of mercury, density = 13.5939 g/cm^3?
b. What is the mass of 25.0 mL octane, density = 0.702 g/cm^3?

90. Calculate these masses.

a. What is the mass of 4.00 cm^3 of sodium, density = 0.97 g/cm^3 ?
b. What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

91. Calculate these volumes.

a. What is the volume of 25 g iodine, density = 4.93 g/cm^3?
b. What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

92. Calculate these volumes.

a. What is the volume of 11.3 g graphite, density = 2.25 g/cm^3?
b. What is the volume of 39.657 g bromine, density = 2.928 g/cm^3?

93. Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.

94. Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.

95. Convert the temperature of the coldest area in a freezer, −10 °F, to degrees Celsius and kelvin.

96. Convert the temperature of dry ice, −77 °C, into degrees Fahrenheit and kelvin.

97. Convert the boiling temperature of liquid ammonia, −28.1 °F, into degrees Celsius and kelvin.

98. The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?

99. The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?

This page titled 1.4: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **1.10: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

1.4.1: Answers to Selected Exercises

1.

Place a glass of water outside. It will freeze if the temperature is below 0 °C.

3.

(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

5.

(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

7.

Macroscopic. The heat required is determined from macroscopic properties.

9.

Liquids can change their shape (flow); solids can’t. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

11.

The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

13.

Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

15.

Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

17.

(a) element; (b) element; (c) compound; (d) mixture; (e) compound; (f) compound; (g) compound; (h) mixture

19.

In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

21.

Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

23.

(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

25.

(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

27.

(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

29.

physical

31.

The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

33.

Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect “cancel” this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

35.

about a yard

37.

(a) kilograms; (b) meters; (c) meters/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

39.

(a) centi-, $\times 10^{-2}$; (b) deci-, $\times 10^{-1}$; (c) Giga-, $\times 10^{9}$; (d) kilo-, $\times 10^{3}$; (e) milli-, $\times 10^{-3}$; (f) nano-, $\times 10^{-9}$; (g) pico-, $\times 10^{-12}$; (h) tera-, $\times 10^{12}$

41.

(a) m = 18.58 g, V = 5.7 mL. (b) d = 3.3 g/mL (c) dioptase (copper cyclosilicate, d = 3.28—3.31 g/mL); malachite (basic copper carbonate, d = 3.25—4.10 g/mL); Paraiba tourmaline (sodium lithium boron silicate with copper, d = 2.82—3.32 g/mL)

43.

(a) displaced water volume = 2.8 mL; (b) displaced water mass = 2.8 g; (c) The block mass is 2.76 g, essentially equal to the mass of displaced water (2.8 g) and consistent with Archimedes’ principle of buoyancy.

45.

(a) 7.04×10^{2}; (b) 3.344×10^{-2}; (c) 5.479×10^{2}; (d) 2.2086×10^{4}; (e) 1.00000×10^{3}; (f) 6.51×10^{-8}; (g) 7.157×10^{-3}

47.

(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

49.

(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

51.

(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

53.

(a) 2.15×10^{5}; (b) 4.2×10^{6}; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

55.

(a) Archer X; (b) Archer W; (c) Archer Y

57.

(a) mfrac; (b) $\frac{0.94635\ \text{L}}{1\ \text{qt}}$; (c) mfrac

59.

$\frac{2.0\ \text{L}}{67.6\ \text{fl oz}} = \frac{0.030\ \text{L}}{1\ \text{fl oz}}$

Only two significant figures are justified.

61.

68–71 cm; 400–450 g

63.

355 mL

65.

8×10^{-4} cm

67.

yes; weight = 89.4 kg

69.

5.0×10^{-3} mL

71.

(a) 1.3×10^{-4} kg; (b) 2.32×10^{8} kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K

73.

45.4 L

75.

1.0160×10^{3} kg

77.

(a) 394 ft; (b) 5.9634 km; (c) 6.0×10^{2}; (d) 2.64 L; (e) 5.1×10^{18} kg; (f) 14.5 kg; (g) 324 mg

79.

0.46 m; 1.5 ft/cubit

81.

Yes, the acid's volume is 123 mL.

83.

62.6 in (about 5 ft 3 in.) and 101 lb

85.

(a) 3.81 cm × 8.89 cm × 2.44 m; (b) 40.6 cm

87.

2.70 g/cm^3

89.

(a) 81.6 g; (b) 17.6 g

91.

(a) 5.1 mL; (b) 37 L

93.

5371 °F, 3239 K

95.

−23 °C, 250 K

97.

−33.4 °C, 239.8 K

99.

113 °F

This page titled 1.4.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

2: Measurements and the Periodic Table

2.1: Measurements
2.2: Measurement Uncertainty, Accuracy, and Precision
2.3: Mathematical Treatment of Measurement Results
2.4: The Periodic Table
2.5: Chemical Formulas
2.6: Atomic Structure and Symbolism
2.6.1: Extra-Early Atomic Theory
2.6.2: Extra-Evolution of Atomic Theory
2.7: Radioactive Decay
2.7.1: Nuclear Equations
2.7.2: Extra-Uses of Radioisotopes
2.7.3: Extra-Biological Effects of Radiation
2.8: Exercises
2.8.1: Answers to Selected Exercises
2.9: Exercises for Nuclear Reactions
2.9.1: Answers to Exercises for Nuclear Reactions

This page titled 2: Measurements and the Periodic Table is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

2.1: Measurements

Learning Objectives

By the end of this section, you will be able to:

- 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 much of the information that informs the hypotheses, theories, and laws describing 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. (Scientific notation is also known as exponential notation; a review of this topic can be found in Appendix B.) 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. A 2-liter bottle of a soft drink contains a volume of beverage that is twice that of the accepted volume of 1 liter. The meat used to prepare a 0.25-pound hamburger weighs one-fourth as much as the accepted weight of 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.

The measurement units for seven fundamental properties ("base units") are listed in Table **2.1.1**. 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. Units for other properties may be derived from these seven base units.

Table **2.1.1**: 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

Everyday measurement units are often defined as fractions or multiples of other units. Milk is commonly packaged in containers of 1 gallon (4 quarts), 1 quart (0.25 gallon), and one pint (0.5 quart). This same approach is used with SI units, 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 **2.1.2**.

Table **2.1.2**: Common Unit Prefixes

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

Prefix	Symbol	Factor	Example
iga			(8,000,000,000 yr)
tera	T	10^{12}	5 terawatts (TW) = 5 x 10^{12} W (5,000,000,000,000 W)

Link to Learning

Need a refresher or more practice with scientific notation? Visit this site to go over the basics of scientific notation.

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 **2.1.1**); 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).

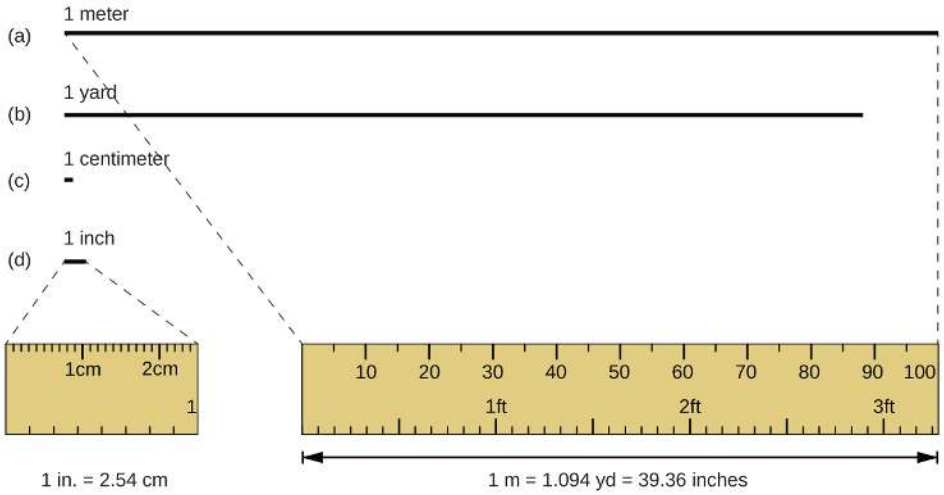


Figure **2.1.1**: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

The standard unit of mass in the SI system is the **kilogram** (kg). The kilogram was previously defined by the International Union of Pure and Applied Chemistry (IUPAC) as the mass of a specific reference object. This object was originally one liter of pure water, and more recently it was a metal cylinder made from a platinum-iridium alloy with a height and diameter of 39 mm (Figure **2.1.2**). In May 2019, this definition was changed to one that is based instead on precisely measured values of several fundamental physical constants.[1]. 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 **2.1.2**: This replica prototype kilogram as previously defined 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 x 10^{-6} and 5 megaseconds = 5,000,000 s = 5 x 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 **2.1.3**). 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 equivalent to a milliliter (mL) and is 1/1000 of a liter.

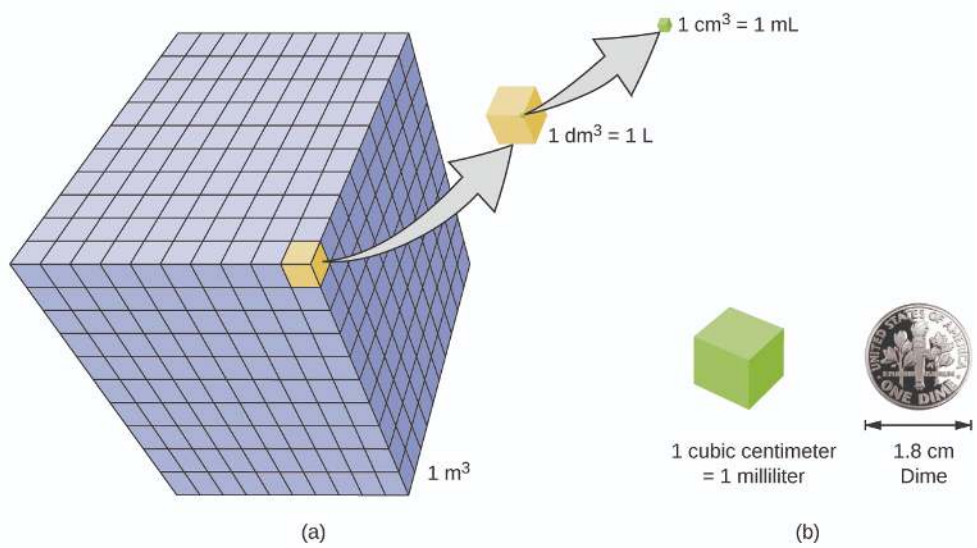


Figure **2.1.3**: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

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 is 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 **2.1.3** shows the densities of some common substances.

Table **2.1.3**: 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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{2.1.1}$$

Example 2.1.1: 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.

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

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

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

Exercise 2.1.1

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
b. 8.91 g/cm^3

Link to Learning

To learn more about the relationship between mass, volume, and density, use this interactive simulator to explore the density of different materials.

Example 2.1.2: Using Displacement of Water to Determine Density

This exercise uses a simulation to illustrate an alternative approach to the determination of density that involves measuring the object's volume via displacement of water. Use the simulator to determine the densities iron and wood.

Solution

Click the "turn fluid into water" button in the simulator to adjust the density of liquid in the beaker to 1.00 g/mL. Remove the red block from the beaker and note the volume of water is 25.5 mL. Select the iron sample by clicking "iron" in the table of materials at the bottom of the screen, place the iron block on the balance pan, and observe its mass is 31.48 g. Transfer the iron block to the beaker and notice that it sinks, displacing a volume of water equal to its own volume and causing the water level to rise to 29.5 mL. The volume of the iron block is therefore:

$$v_{\text{iron}} = 29.5mL - 25.5mL = 4.0mL$$

The density of the iron is then calculated to be:

$$\text{density } = \frac{\text{mass}}{\text{volume}} = \frac{31.48\ \text{g}}{4.0\ \text{mL}} = 7.9\ \text{g/mL}$$

Remove the iron block from the beaker, change the block material to wood, and then repeat the mass and volume measurements. Unlike iron, the wood block does not sink in the water but instead floats on the water's surface. To measure its volume, drag it beneath the water's surface so that it is fully submerged.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{1.95\,\text{g}}{3.0\,\text{mL}} = 0.65\,\text{g/mL}$$

Note: The sink versus float behavior illustrated in this example demonstrates the property of “buoyancy”.

? Exercise 2.1.2

Following the water displacement approach, use the simulator to measure the density of the foam sample.

Answer

0.230 g/mL

Footnotes

- 1For details see https://www.nist.gov/pml/weights-and.../si-units-mass

---

This page titled 2.1: Measurements is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **1.4: Measurements** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.2: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

By the end of this section, you will be able to:

- 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**. By counting the eggs in a carton, one can determine *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.

2.2.1: 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.

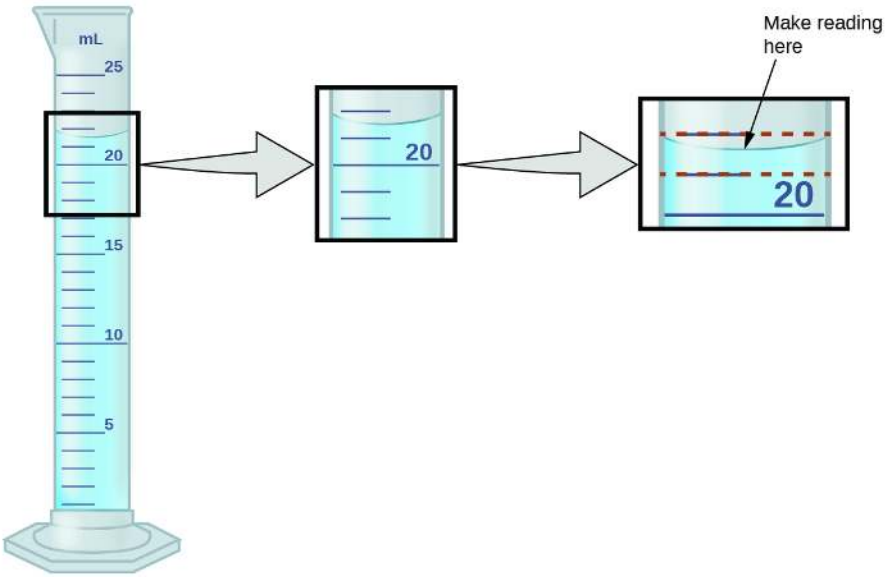
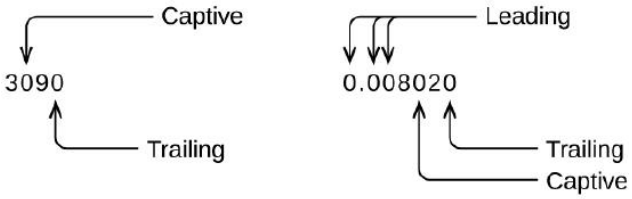


Figure **2.2.1**: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in Figure **2.2.1**. 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 the coin is weighed on a more sensitive balance, the mass might be 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.

A measurement result is properly reported when its significant digits accurately represent the certainty of the measurement process. 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.

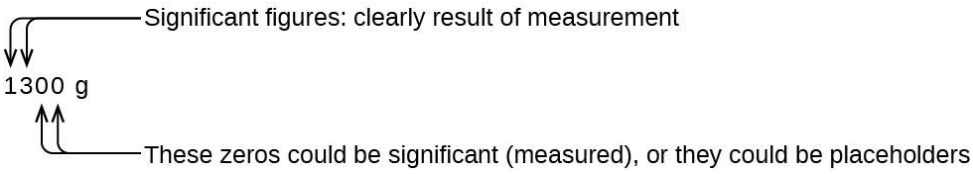


Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



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 when evaluating 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 $3.17\ 10^8$ people.

2.2.2: 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. Take the uncertainty in 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 adding or subtracting numbers, round the result to the same number of decimal places as the number with the least number of decimal places (the least certain value in terms of addition and subtraction).
2. When multiplying or dividing numbers, round the result to the same number of digits as the number with the least number of significant figures (the least certain 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, “round down” and leave the retained digit unchanged; if it is more than 5, “round up” and increase the retained digit by 1. If the dropped digit is 5, and it’s either the last digit in the number or it’s followed only by zeros, round up or down, whichever yields an even value for the retained digit. If any nonzero digits follow the dropped 5, round up. (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 a nonzero digit follows it)
- 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 2.2.1: 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 2.2.1

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
b. 0.00387
c. 421.2
d. 28,684

Example 2.2.2: Addition and Subtraction with Significant Figures

Rule: When adding or subtracting numbers, round the result to the same number of decimal places as the number with the fewest decimal places (i.e., the least certain 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)

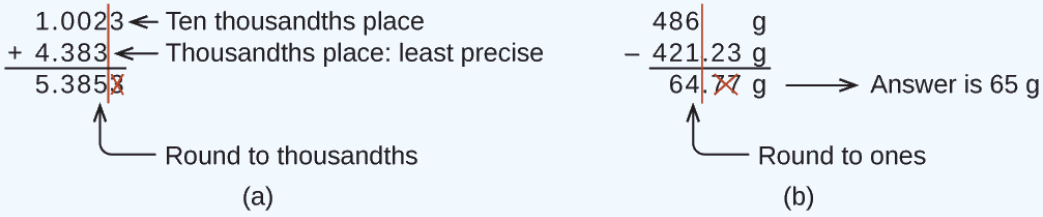
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

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 2.2.2

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

Answer

a. 2.64 mL
b. 0.658 m

Example 2.2.3: Multiplication and Division with Significant Figures

Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain 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)

$$\underbrace{0.6238\,\text{cm}}_{\text{four significant figures}} \times \underbrace{6.6\,\text{cm}}_{\text{two significant figures}} = 4.11708\,\text{cm}^2 \rightarrow \underbrace{4.1\,\text{cm}^2}_{\text{round to two significant figures}}$$

(b)

$$\underbrace{421.23\,\text{g}}_{\text{five significant figures}} \div \underbrace{486\,\text{mL}}_{\text{three significant figures}} = 0.866728\ldots\,\text{g/mL} \rightarrow \underbrace{0.867\,\text{g/mL}}_{\text{round to three significant figures}}$$

Exercise 2.2.3

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

Answer

a. 0.747 cm^2
b. 0.9884 m/s

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

Example 2.2.4: 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

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

Exercise 2.2.4

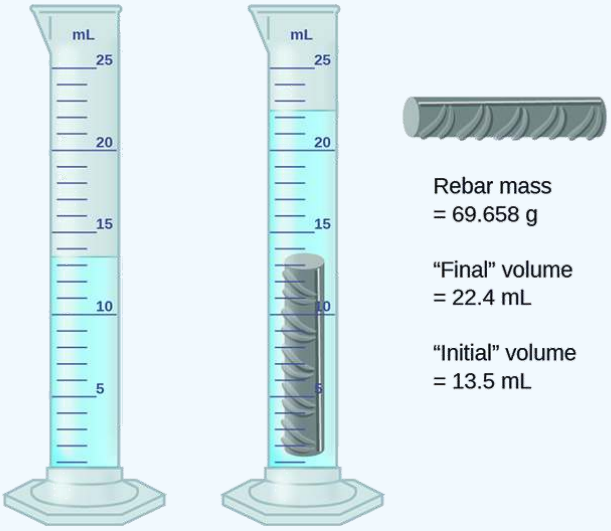
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 2.2.5: Experimental Determination of Density Using Water Displacement

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 2.2.5

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

19 g/cm^3

It is likely gold; the right appearance for gold and very close to the known density of gold at **19.3 g/cm^3**

2.2.3: Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to evaluate 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 **2.2.2**).

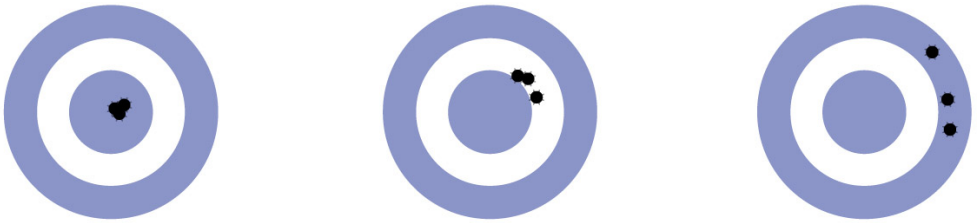


Figure **2.2.2**: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither 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 **2.2.1**.

Table **2.2.1**: 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).

This page titled 2.2: Measurement Uncertainty, Accuracy, and Precision is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **1.5: Measurement Uncertainty, Accuracy, and Precision** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.3: Mathematical Treatment of Measurement Results

Learning Objectives

By the end of this section, you will be able to:

- 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:

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

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

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

(For this and the next calculation, assume the trailing zeros are significant digits.) 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 among 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:

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

The time can then be computed as:

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

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.

2.3.1: 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,

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

Several other commonly used conversion factors are given in Example **2.3.1**.

Example **2.3.1**: 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 a quantity (such as distance in inches) is multiplied by an appropriate unit conversion factor, the quantity is converted 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:

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

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 . Just as for numbers, a ratio of identical units is also numerically equal to one, and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to "cancel.") Dimensional analysis may be used to confirm the proper application of unit conversion factors as demonstrated in the following example.

✔ Example 2.3.1: 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 (Example **2.3.1**).

Solution

Given the conversion factor, the mass in ounces may be derived using an equation similar to the one used for converting length from inches to centimeters.

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

The unit conversion factor may be represented as:

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

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

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

? Exercise 2.3.1

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 ensure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 2.3.2: Computing Quantities from Measurement Results and Known Mathematical Relations

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 $\text{density} = \frac{\text{mass}}{\text{volume}}$, 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 Example 2.3.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. Mass may be converted from pounds to grams as follows:

$$9.26 \cancel{\text{lb}} \times \left(\frac{453.59\,\text{g}}{1\,\cancel{\text{lb}}} \right) = 4.20 \times 10^3\,\text{g}$$

Volume may be converted from quarts to milliliters via two steps:

Step 1: Convert quarts to liters.

$$4.00\,\cancel{\text{qt}} \times \left(\frac{1\,\text{L}}{1.0567\,\cancel{\text{qt}}} \right) = 3.78\,\text{L}$$

Step 2: Convert liters to milliliters.

$$3.78\,\cancel{\text{L}} \times \left(\frac{1000\,\text{mL}}{1\,\cancel{\text{L}}} \right) = 3.78 \times 10^3\,\text{mL}$$

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 2.3.2

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

Answer

2.956×10^{-2} L

Example 2.3.3: Computing Quantities from Measurement Results and Known Mathematical Relations

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) First convert distance from kilometers to miles:

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

and then convert volume from liters to gallons:

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

Finally,

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

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:

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

? Exercise 2.3.3

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
b. $62

2.3.2: 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 liquid in a common glass thermometer changes its volume as the temperature changes, and the position of the trapped liquid's surface along a printed scale may be used as a measure of temperature.

Temperature scales are defined relative to selected reference temperatures: 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:

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

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:

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

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:

$$b = y - mx = 32^\circ F - \frac{9^\circ F}{5^\circ C} \times 0^\circ C = 32^\circ F$$

The equation relating the temperature (T) scales is then:

$$T^\circ F = \left(\frac{9^\circ F}{5^\circ C} \times T^\circ C\right) + 32^\circ F$$

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

$$T^\circ F = \left(\frac{9}{5} \times T^\circ C\right) + 32$$

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

$$T^\circ F = \left(\frac{9}{5} \times T^\circ C\right) + 32$$

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. Since the kelvin temperature scale is absolute, a degree symbol is not included in the unit abbreviation, K. 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 is 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 . Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

$$T_K = T^\circ C + 273.15$$
$$T^{\circ C} = T_K - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure **2.3.1**: shows the relationship among the three temperature scales.

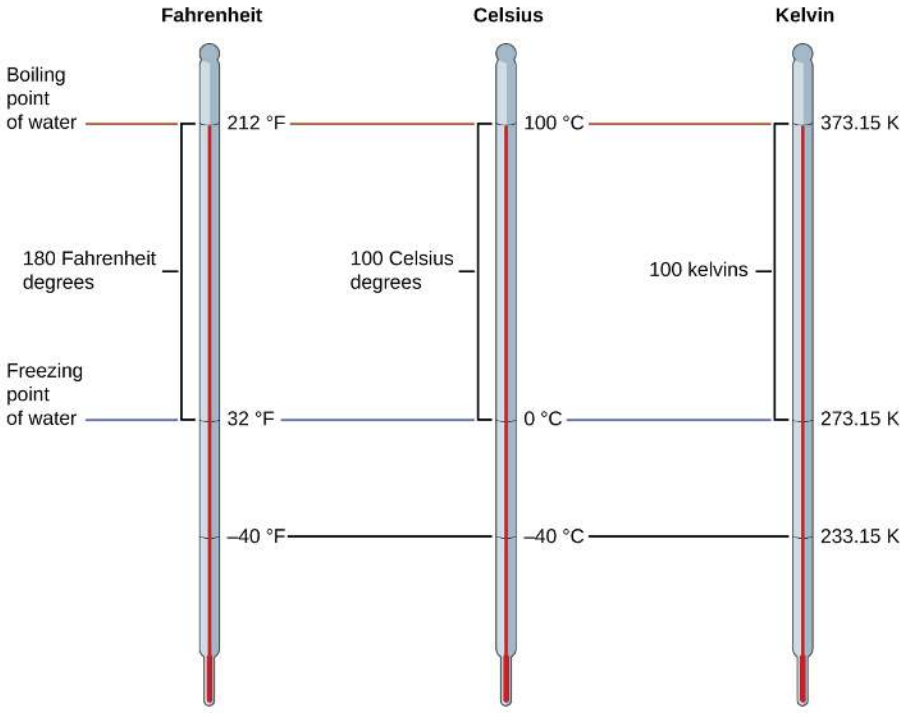


Figure **2.3.1**: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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 2.3.4: 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

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

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

? Exercise 2.3.1

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

✔ Example 2.3.5: 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

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

$$K = {}^\circ C + 273.15 = \frac{5}{9}\,({}^\circ F - 32) = \frac{5}{9}(450 - 32) + 273.15 = 505.4 K \longrightarrow 5.1 \times 10^2 K$$

Exercise 2.3.1

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

2.3.3: Footnotes

- 2 Strictly speaking, the ounce and pound are units of weight, *W* (a force equal to the product of mass and gravitational acceleration, *W* = *mg*). The conversion relations in this table are commonly used to equate masses and weight assuming a nominal value for *g* at the surface of the earth.

This page titled 2.3: Mathematical Treatment of Measurement Results is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **1.6: Mathematical Treatment of Measurement Results** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.4: The Periodic Table

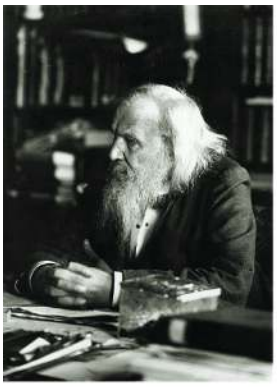
Learning Objectives

By the end of this section, you will be able to:

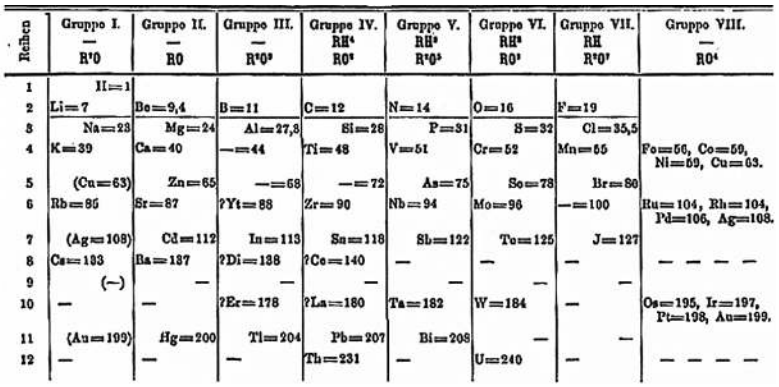
- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

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 **2.4.1**).



(a)



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	—	— — — —

(b)

Figure **2.4.1**: (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 **2.4.2**). 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.

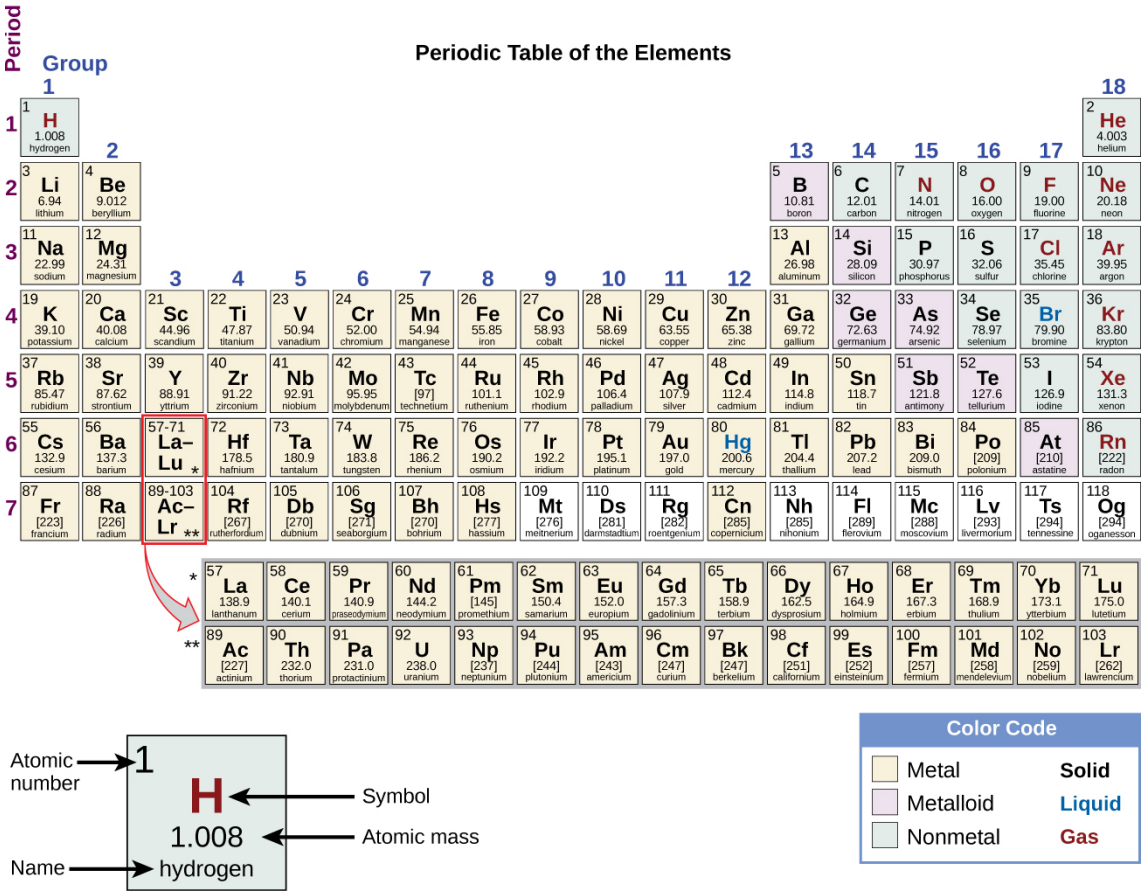


Figure **2.4.2**: Elements in the periodic table are organized according to their properties.

Even after the periodic nature of elements and the table itself were widely accepted, gaps remained. Mendeleev had predicted, and others including Henry Moseley had later confirmed, that there should be elements below Manganese in Group 7. German chemists Ida Tacke and Walter Noddack set out to find the elements, a quest being pursued by scientists around the world. Their method was unique in that they did not only consider the properties of manganese, but also the elements horizontally adjacent to the missing elements 43 and 75 on the table. Thus, by investigating ores containing minerals of ruthenium (Ru), tungsten (W), osmium (Os), and so on, they were able to identify naturally occurring elements that helped complete the table. Rhenium, one of their discoveries, was one of the last natural elements to be discovered and is the last stable element to be discovered. (Francium, the last natural element to be discovered, was identified by Marguerite Perey in 1939.)

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[3]; 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 **2.4.3**). 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.

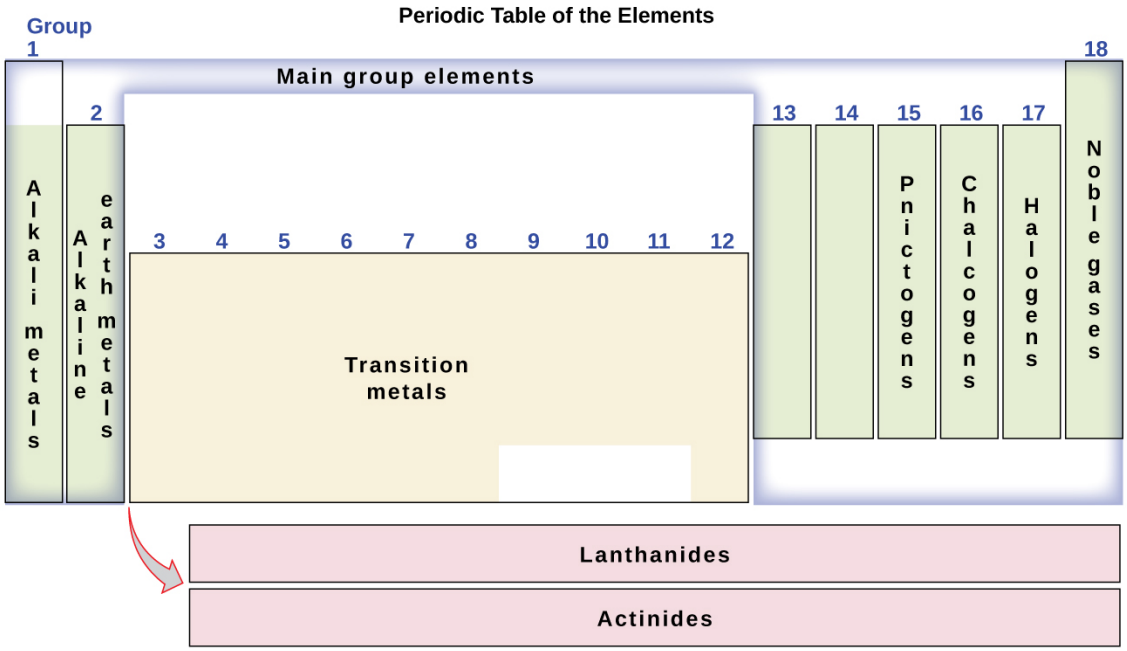


Figure **2.4.3**: The periodic table organizes elements with similar properties into groups.

Link to Learning

Click on this link for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this one that shows photos of all the elements.

Example 2.4.1: 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 2.4.1

Give the group name for each of the following elements:

a. krypton
b. selenium

c. barium
d. lithium

Answer

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

As you will learn in your further study of chemistry, elements in groups often behave in a somewhat similar manner. This is partly due to the number of electrons in their outer shell and their similar readiness to bond. These shared properties can have far-ranging implications in nature, science, and medicine. For example, when Gertrude Elion and George Hitchens were investigating ways to interrupt cell and virus replication to fight diseases, they utilized the similarity between sulfur and oxygen (both in Group 16) and their capacity to bond in similar ways. Elion focused on purines, which are key components of DNA and which contain oxygen. She found that by introducing sulfur-based compounds (called purine analogues) that mimic the structure of purines, molecules within DNA would bond to the analogues rather than the "regular" DNA purine. With the normal DNA bonding and structure altered, Elion successfully interrupted cell replication. At its core, the strategy worked because of the similarity between sulfur and oxygen. Her discovery led directly to important treatments for leukemia. Overall, Elion's work with George Hitchens not only led to more treatments, but also changed the entire methodology of drug development. By using specific elements and compounds to target specific aspects of tumor cells, viruses, and bacteria, they laid the groundwork for many of today's most common and important medicines, used to help millions of people each year. They were awarded the Nobel Prize in 1988.

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 (an approximate atomic mass) of the most stable isotope of that element.

2.4.1: Footnotes

- 3Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group’s elements are provided in a chapter on transition metals and coordination chemistry.

This page titled 2.4: The Periodic Table is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.5: The Periodic Table** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.5: Chemical Formulas

Learning Objectives

By the end of this section, you will be able to:

- 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 **2.5.1**). 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.

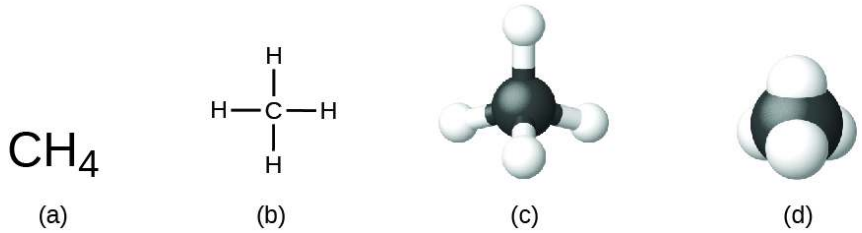


Figure **2.5.1** : A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

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 **2.5.2**).

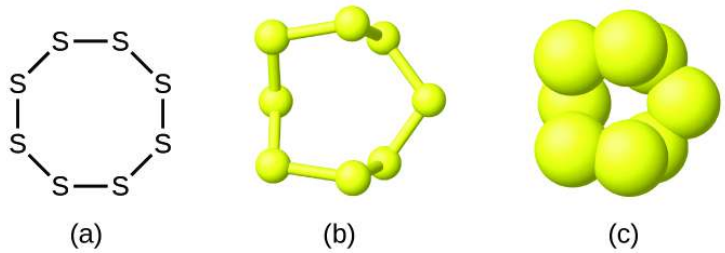


Figure **2.5.2** : A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

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 **2.5.3**).

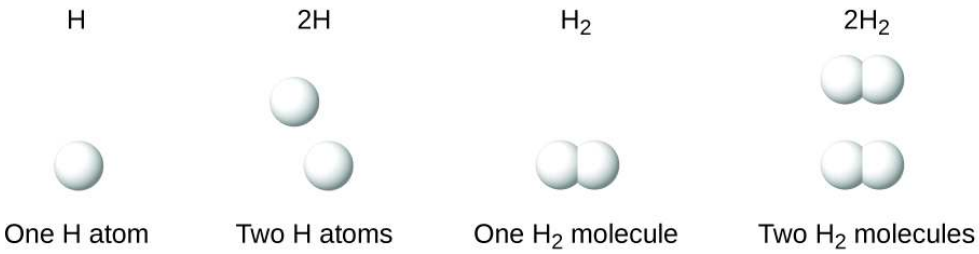


Figure **2.5.3** : The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

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 **2.5.4**).

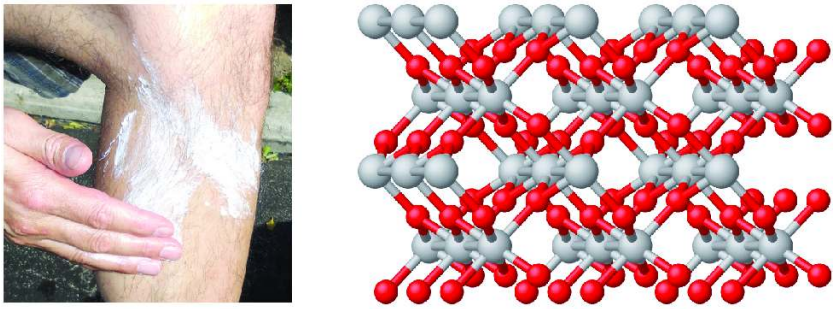


Figure **2.5.4** : (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr)

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 **2.5.5**).

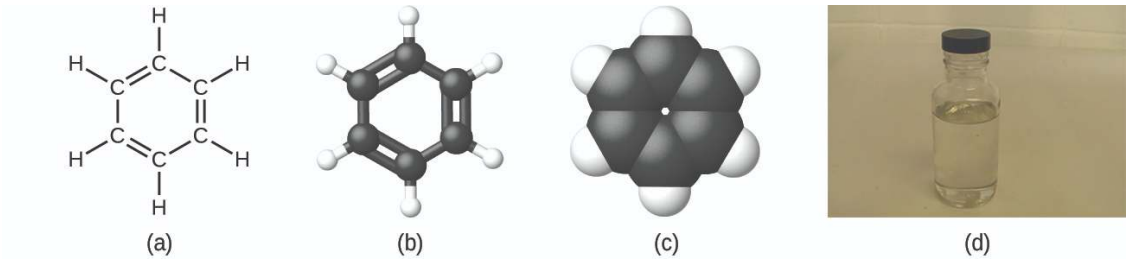
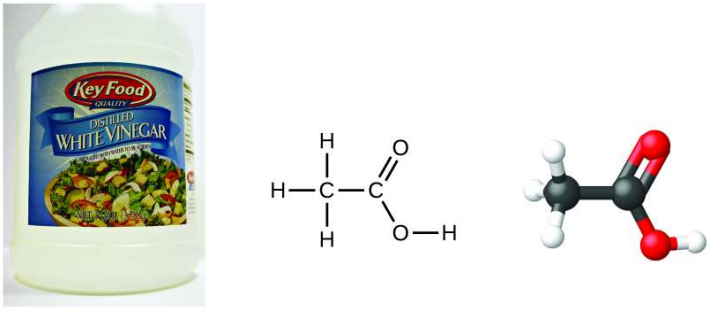


Figure **2.5.5** : Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

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 **2.5.6**) 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.



(a) (b) (c)

Figure **2.5.6**: (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 2.5.1: 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 2.5.1

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

Link to Learning

You can explore molecule building using an online simulation.

Portrait of a Chemist: Lee Cronin

What is it that chemists do? According to Lee Cronin (Figure **2.5.7**), chemists make very complicated molecules by "chopping up" small molecules and "reverse engineering" them. He wonders if we could "make a really cool universal chemistry set" by what he calls "app-ing" chemistry. Could we "app" chemistry?



Figure 2.5.7: Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. The youngest chair at the University of Glasgow, Lee runs a large research group, collaborates with many scientists worldwide, has published over 250 papers in top scientific journals, and has given more than 150 invited talks. His research focuses on complex chemical systems and their potential to transform technology, but also branches into nanoscience, solar fuels, synthetic biology, and even artificial life and evolution. (credit: image courtesy of Lee Cronin)

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical "inks" with a 3D printer capable of fabricating a reaction apparatus (tiny test tubes, beakers, and the like) to fashion a "universal toolkit of chemistry." This toolkit could be used to create custom-tailored drugs to fight a new superbug or to "print" medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, "What Apple did for music, I'd like to do for the discovery and distribution of prescription drugs."[2] View his full talk at the TED website.

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 a 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 2.5.8). 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.

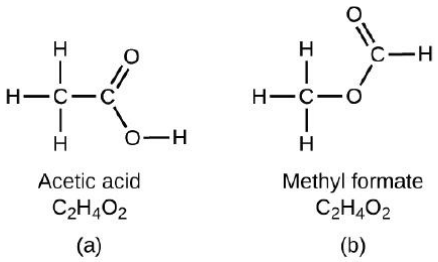


Figure 2.5.8: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 2.5.9). 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.

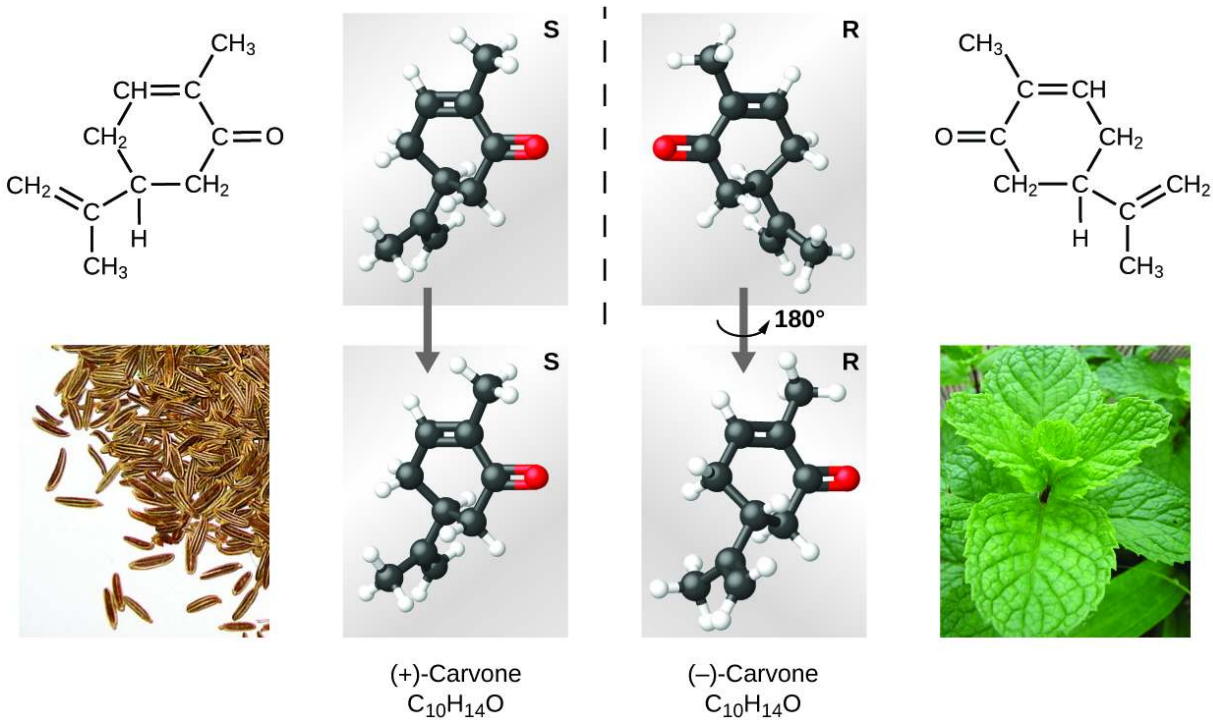


Figure **2.5.0**: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Link to Learning

Select this link to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled "Mirror Molecule: Carvone").

2.5.1: Footnotes

- 2Lee Cronin, "Print Your Own Medicine," Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.

This page titled 2.5: Chemical Formulas is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.4: Chemical Formulas** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.6: Atomic Structure and Symbolism

Learning Objectives

By the end of this section, you will be able to:

- 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 **2.6.1**).



Figure **2.6.1**: 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 $\frac{1}{12}$ 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 **2.6.1**. (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 12.00 amu. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table **2.6.1**: 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.

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

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 2.6.1: 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 2.6.2).



(a) (b)

Figure 2.6.2: (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 2.6.1

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+

2.6.1: 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 **2.6.3**). 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 **2.6.3**: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The symbols for several common elements and their atoms are listed in Table **2.6.2**. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. 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 (also found in Appendix A).

Table **2.6.2**: 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 occasionally 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. Element 109 was named in honor of Lise Meitner, who discovered nuclear fission, a phenomenon that would have world-changing impacts; Meitner also contributed to the discovery of some major isotopes, discussed immediately below.

Link to Learning

Visit this site to learn more about IUPAC, the International Union of Pure and Applied Chemistry, and explore its periodic table.

2.6.2: 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 **2.6.4**). 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.

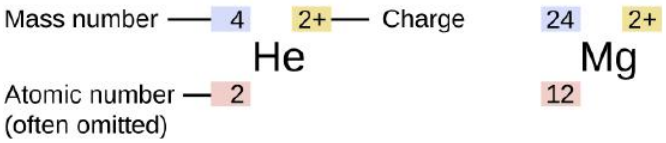


Figure **2.6.4**: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table **2.6.3**. 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 **2.6.3**: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}H$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}H$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}H$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}He$	2	2	1	3.01603	0.00013
	$^{4}_{2}He$	2	2	2	4.0026	100
lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}Be$	4	4	5	9.0122	100
boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}N$	7	7	7	14.0031	99.63
	$^{15}_{7}N$	7	7	8	15.0001	0.37
oxygen	$^{16}_{81}O$	8	8	8	15.9949	99.757
	$^{17}_{81}O$	8	8	9	16.9991	0.038
	$^{18}_{81}O$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}F$	9	9	10	18.9984	100
neon	$^{20}_{10}Ne$	10	10	10	19.9924	90.48
	$^{21}_{10}Ne$	10	10	11	20.9938	0.27
	$^{22}_{10}Ne$	10	10	12	21.9914	9.25

Link to Learning

Use this Build an Atom simulator to build atoms of the first 10 elements, see which isotopes exist, check nuclear stability, and gain experience with isotope symbols.

2.6.3: 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.

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

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are $^{10}\mathbf{B}$ with a mass of 10.0129 amu, and the remaining 80.1% are $^{11}\mathbf{B}$ 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 2.6.2: 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 2.6.2

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 2.6.3: 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.

$$\text{average mass } = \left(\text{ fraction of } {}^{35}Cl \times \text{ mass of } {}^{35}Cl\right) + \left(\text{ fraction of } {}^{37}Cl \times \text{ mass of } {}^{37}Cl\right)$$

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:

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

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 2.6.3

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

Link to Learning

Visit this site to make mixtures of the main isotopes of the first 18 elements, gain experience with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

As you will learn, isotopes are important in nature and especially in human understanding of science and medicine. Let's consider just one natural, stable isotope: Oxygen-18, which is noted in the table above and is referred to as one of the environmental isotopes. It is important in paleoclimatology, for example, because scientists can use the ratio between Oxygen-18 and Oxygen-16 in an ice core to determine the temperature of precipitation over time. Oxygen-18 was also critical to the discovery of metabolic pathways and the mechanisms of enzymes. Mildred Cohn pioneered the usage of these isotopes to act as tracers, so that researchers could follow their path through reactions and gain a better understanding of what is happening. One of her first discoveries provided insight into the phosphorylation of glucose that takes place in mitochondria. And the methods of using isotopes for this research contributed to entire fields of study.

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 2.6.5), 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 rolling

past a magnet is deflected to a lesser extent that that of a small steel ball). 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.

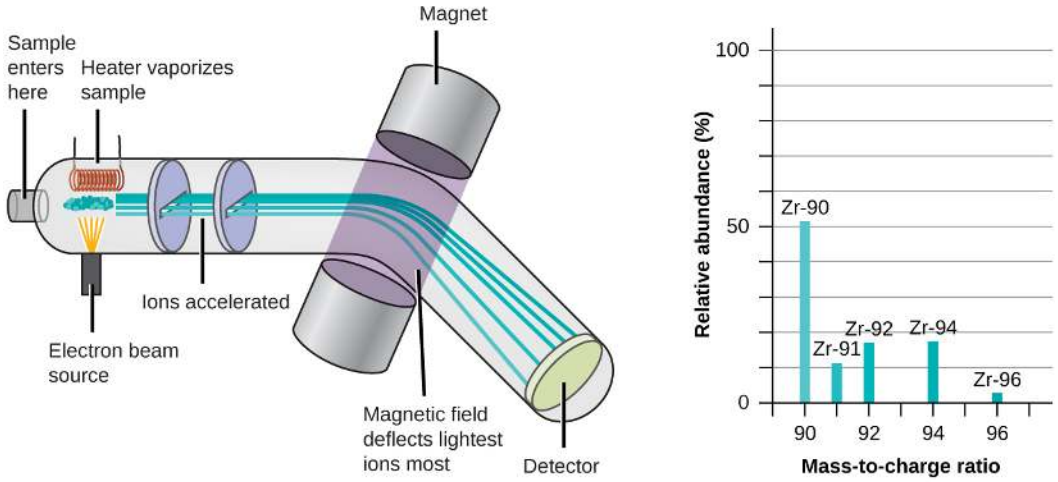


Figure 2.6.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

Link to Learning

See an animation that explains mass spectrometry. Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

This page titled 2.6: Atomic Structure and Symbolism is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.3: Atomic Structure and Symbolism** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.6.1: Extra-Early Atomic Theory

Learning Objectives

By the end of this section, you will be able to:

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure **2.6.1.1**). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

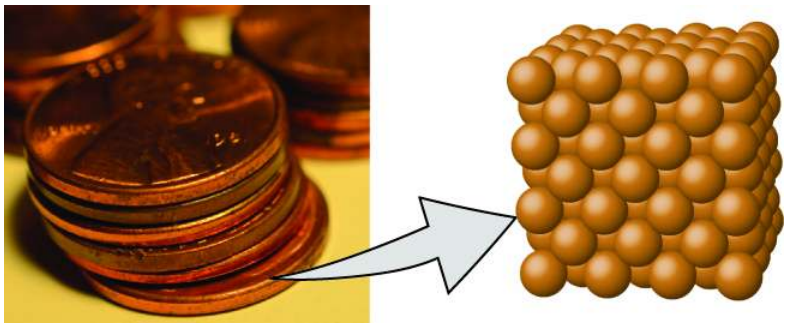


Figure **2.6.1.1**: A pre-1982 copper penny (left) contains approximately 3 10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure **2.6.1.2**).

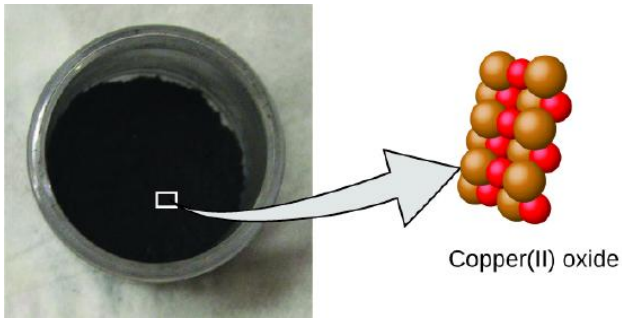


Figure **2.6.1.2**: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure **2.6.1.3**).

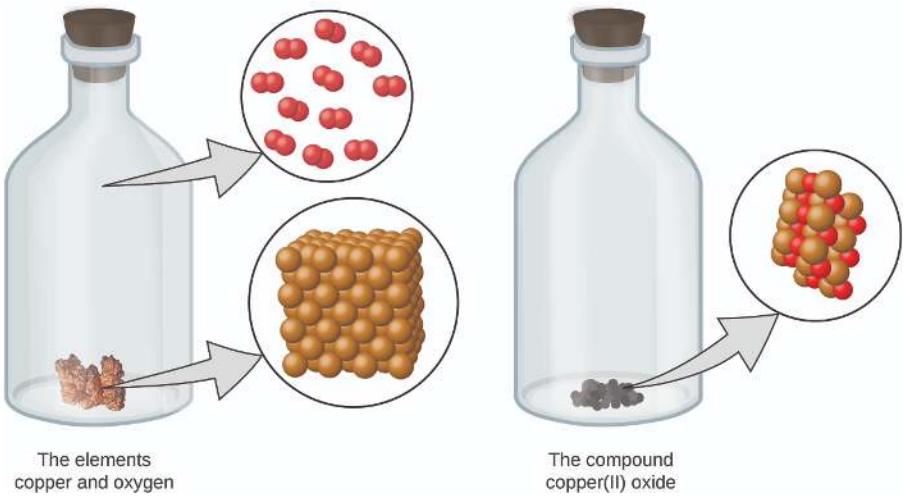
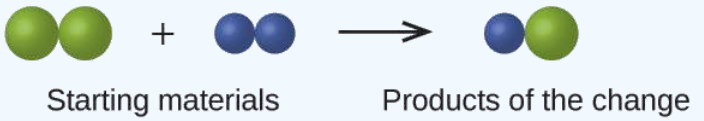


Figure **2.6.1.3**: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php)

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

✔ Example 2.6.1.1: Testing Dalton's Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

? Exercise 2.6.1.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



Answer

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 2.1.

Table 2.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	
B	22.33 g	4.19 g	
C	19.40 g	3.64 g	

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure **2.6.1.4**).

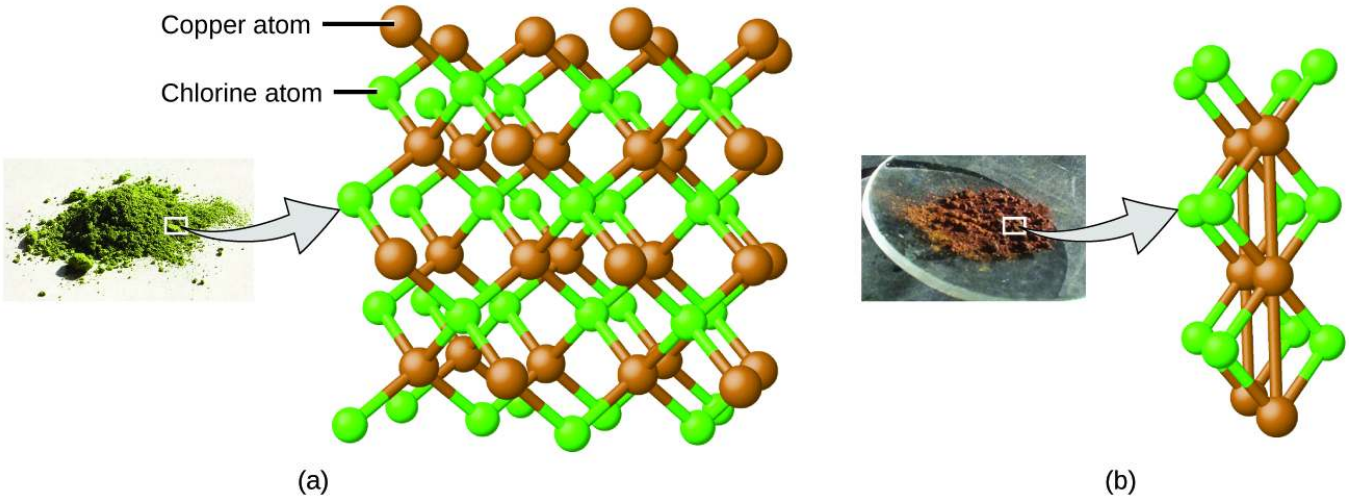


Figure **2.6.1.4**: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

Example 2.6.1.2: Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of oxygen to carbon is:

In compound B, the mass ratio of oxygen to carbon is:

The ratio of these ratios is:

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much oxygen per amount of carbon (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO_2.

Exercise 2.6.1.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer

In compound X, the mass ratio of carbon to hydrogen is In compound Y, the mass ratio of carbon to hydrogen is The ratio of these ratios is This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

This page titled 2.6.1: Extra-Early Atomic Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.1: Early Ideas in Atomic Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.6.2: Extra-Evolution of Atomic Theory

Learning Objectives

By the end of this section, you will be able to:

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Define isotopes and give examples for several elements

If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure **2.6.2.1**).

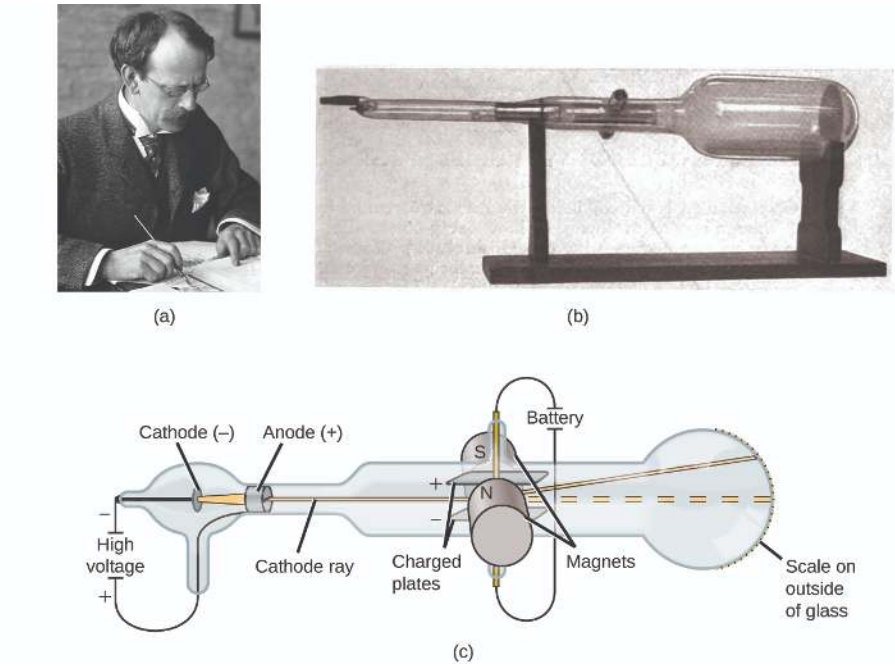


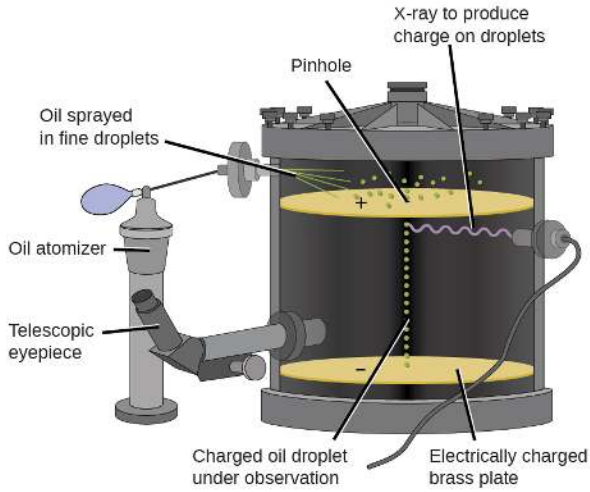
Figure **2.6.2.1**: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "*electr*ic i*on*."

Link to Learning

Click here to hear Thomson describe his discovery in his own voice.

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure **2.6.2.2**).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure **2.6.2.2**: Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6 10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6 10^{-19} C), two electrons (2 times 1.6 10^{-19} C), three electrons (3 times 1.6 10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan’s research, and the charge-to-mass ratio was already known due to Thomson’s research (1.759 10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure **2.6.2.3**).

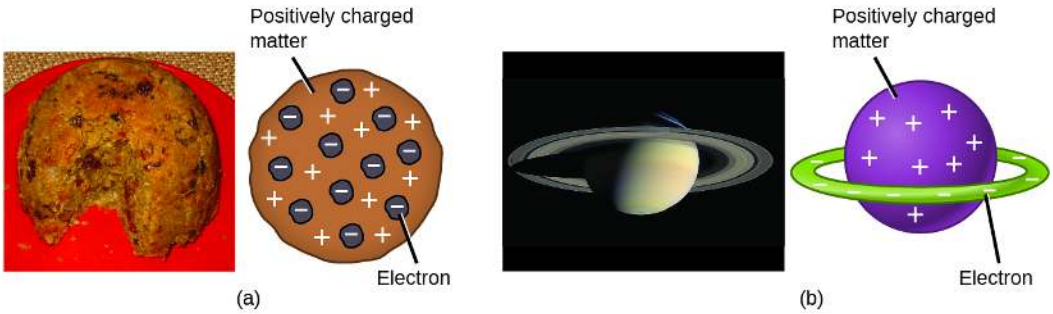


Figure **2.6.2.3**: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons)

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure **2.6.2.4**). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."[1]

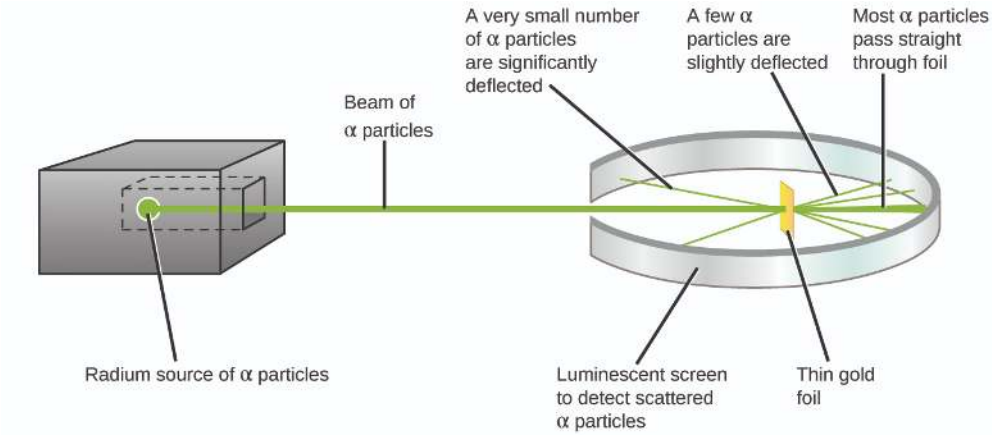


Figure **2.6.2.4**: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

Link to Learning

View this simulation of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of α particles to see how that affects the scattering pattern.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure **2.6.2.5**). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

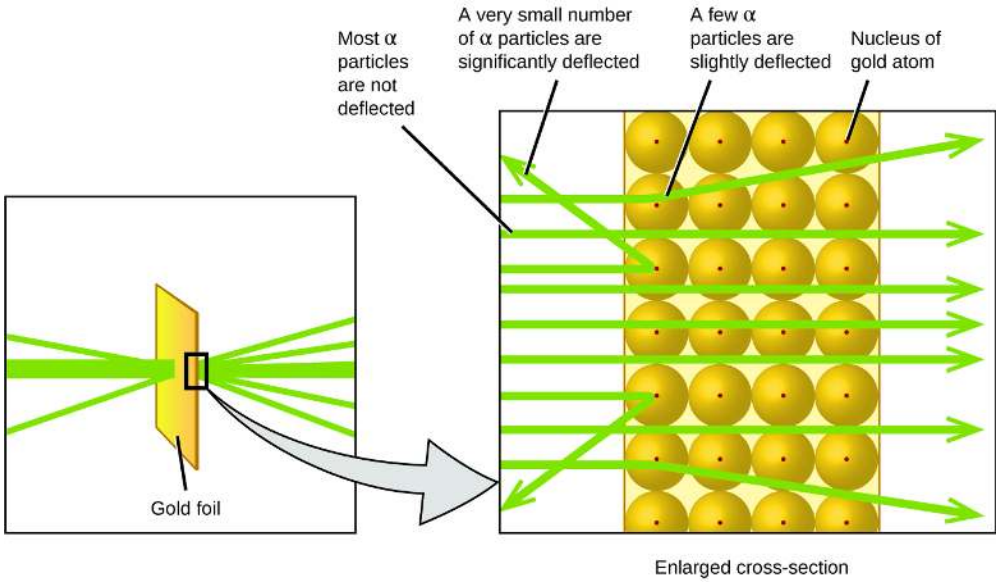


Figure **2.6.2.5**: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

Link to Learning

The Rutherford Scattering simulation allows you to investigate the differences between a "plum pudding" atom and a Rutherford atom by firing α particles at each type of atom.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

2.6.2.1: Footnotes

- 1Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

This page titled 2.6.2: Extra-Evolution of Atomic Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.2: Evolution of Atomic Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.7: Radioactive Decay

Learning Objectives

By the end of this section, you will be able to:

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure **2.7.1**).

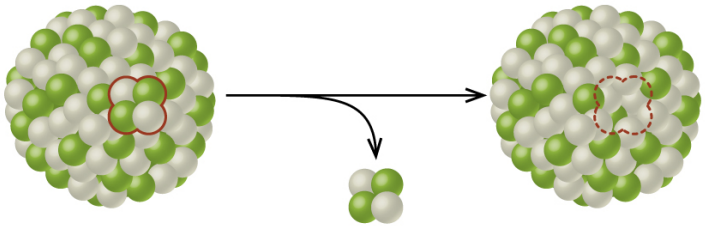


Figure **2.7.1**: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

Link to Learning

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

2.7.1: Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure **2.7.2**) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

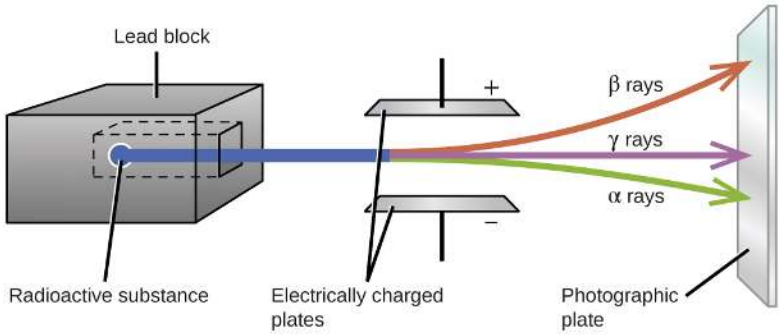


Figure **2.7.2**: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb}$$

or

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha^{+}_{82}{}^{206}\ \text{Pb}$$

Alpha decay occurs primarily in heavy nuclei ($A > 200$, $Z > 83$). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to Figure 21.2), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron (i.e., a β particle) from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\text{e} + {}^{131}_{54}\text{Xe}$$

or

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\beta^{+}_{54}{}^{131}\ \text{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\text{Co}^{*} \longrightarrow {}^{0}_{0}\gamma^{+}_{27}{}^{60}\ \text{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^{+} decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\text{e} + {}^{15}_{7}\text{N}$$

or

$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\beta^{+}_{7}{}^{15}\ \text{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure **2.7.3** summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

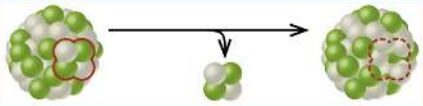
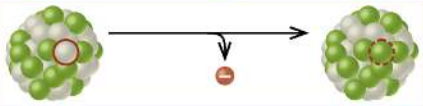
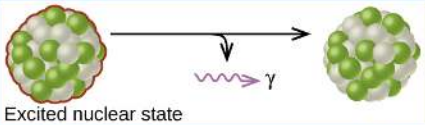
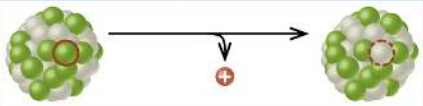
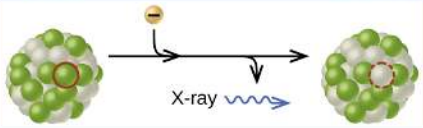
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{A-4}_{Z-2}\mathrm{Y}$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Z+1}\mathrm{Y}$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}\mathrm{Y}$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{+1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1

Figure **2.7.3**: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

Chemistry in Everyday Life: PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (Figure **2.7.4**). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

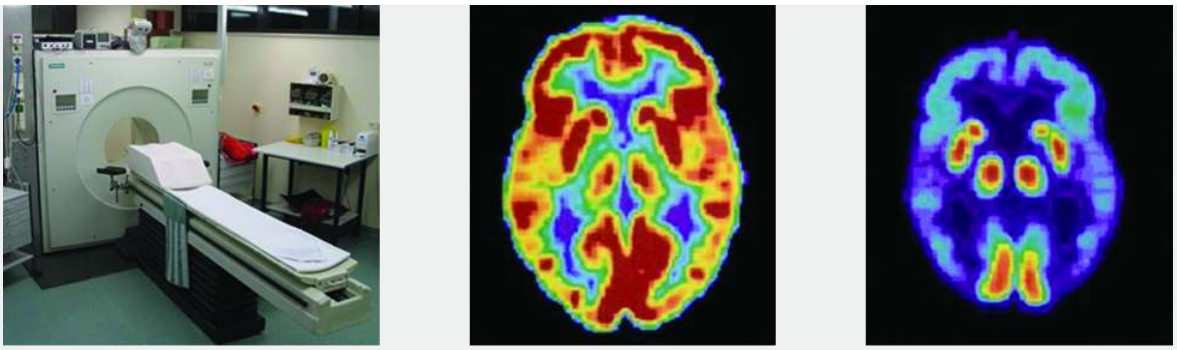


Figure **2.7.4**: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of \(\ce{^{18}O}\)

$$^{18}_{8}\mathrm{O} + {}_{1}{}^{1}\mathrm{p} \longrightarrow {}^{18}_{9}\mathrm{F} + {}_{0}{}^{1}\mathrm{n}$$

and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The $^{18}\mathrm{F}$ emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

2.7.2: Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure **2.7.5**). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

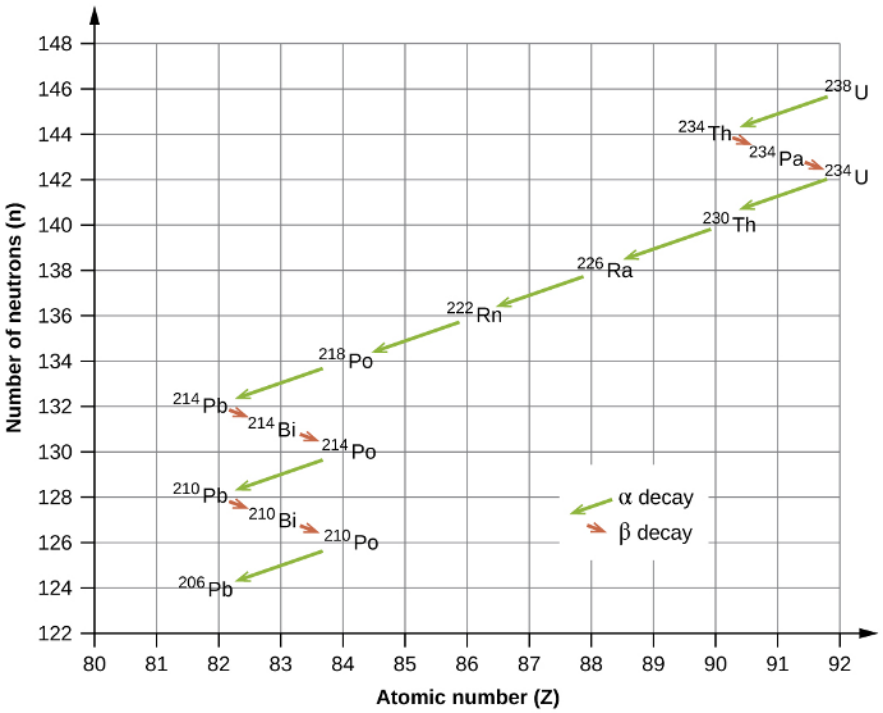


Figure **2.7.5**: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

2.7.3: Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years. In a given cobalt-60 source, since half of the nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

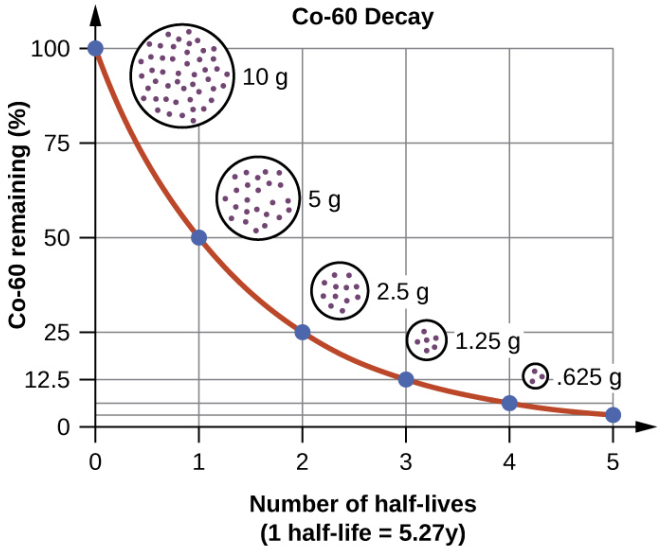


Figure **2.7.6**: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\mathrm{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\mathrm{Ra}$ is 24,000 years; $^{222}_{86}\mathrm{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table **2.7.1**, and others are listed in Appendix M.

Table **2.7.1**: Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

2.7.4: Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

2.7.4.1: Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\mathrm{C}$ which constitutes about 99% of the carbon on earth; $^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}CO_2$ to $^{12}_{6}CO_2$ depends on the ratio of $^{14}_{6}CO$ to $^{12}_{6}CO$ in the atmosphere. The natural abundance of $^{14}_{6}CO$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}CO_2$ and $^{14}_{6}CO_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}C : ^{12}_{6}C$ ratio found in a living plant is the **same** as the $^{14}_{6}C : ^{12}_{6}C$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}C$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + ^{0}_{-1}\text{e}$$

Thus, the ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure **2.7.7**: visually depicts this process.

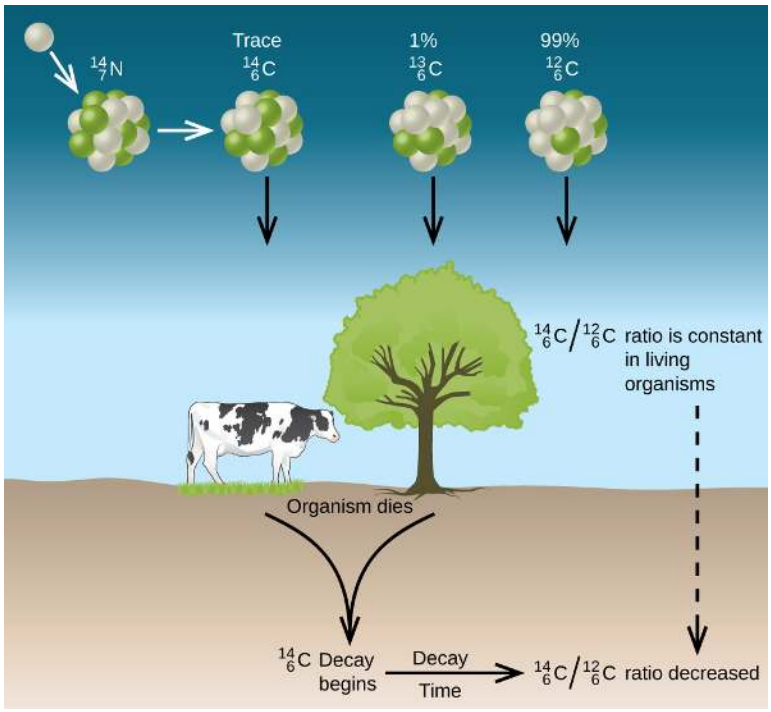


Figure **2.7.7**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of being 5730 years, if the ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Link to Learning

Visit this website to perform simulations of radiometric dating.

There have been some significant, well-documented changes to the $^{14}_{6}C : ^{12}_{6}C$ ratio. The accuracy of a straightforward application of this technique depends on the $^{14}_{6}C : ^{12}_{6}C$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $^{12}_{6}C$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $^{14}_{6}C$ has decayed), the ratio of $^{14}_{6}C : ^{12}_{6}C$ in the atmosphere may be changing. This manmade increase in $^{12}_{6}C$ in the atmosphere causes the $^{14}_{6}C : ^{12}_{6}C$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate

correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

This page titled 2.7: Radioactive Decay is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **21.3: Radioactive Decay** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.7.1: Nuclear Equations

Learning Objectives

By the end of this section, you will be able to:

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure **2.7.1.1**. Protons ($_1^1\mathrm{p}$, also represented by the symbol $_1^1\mathrm{H}$) and neutrons ($_0^1\mathrm{n}$) are the constituents of atomic nuclei, and have been described previously. **Alpha particles** ($_2^4\mathrm{He}$, also represented by the symbol $_2^4\alpha$) are high-energy helium nuclei. **Beta particles** ($_{-1}^0\beta$, also represented by the symbol $_1^0\mathrm{e}$) are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** ($_{+1}^0\mathrm{e}$, also represented by the symbol $_1^0\beta$) are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized $_2^4\mathrm{He}$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Name	Symbol(s)	Representation	Description
Alpha particle	$_2^4\mathrm{He}$ or $_2^4\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$_{-1}^0\mathrm{e}$ or $_{-1}^0\beta$		(High-energy) electrons
Positron	$_{+1}^0\mathrm{e}$ or $_{+1}^0\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	$_1^1\mathrm{H}$ or $_1^1\mathrm{p}$		Nuclei of hydrogen atoms
Neutron	$_0^1\mathrm{n}$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Figure **2.7.1.1**: Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays** (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$$_{-1}{}^0\mathrm{e} + {}_{+1}{}^0\mathrm{e} \longrightarrow \gamma + \gamma$$

As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are a type of high energy electromagnetic radiation produced when a nucleus undergoes a transition

from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of nucleons (subatomic particles within the atoms' nuclei) rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of ${}^{14}_{7}\mathrm{N}$ and ${}^{4}_{2}\mathrm{He}$ if we knew that a proton, ${}^{1}_{1}\mathrm{H}$, were one of the two products. Example **2.7.1.1** shows how we can identify a nuclide by balancing the nuclear reaction.

Example 2.7.1.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 (${}^{25}_{12}\mathrm{Mg}$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$ {}^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{1}_{1}\mathrm{H} + {}^{A}_{Z}\mathrm{X} $$

where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$ 25 + 4 = A + 1 $$

or $A = 28$.

Similarly, the charges must balance, so:

$$ 12 + 2 = Z + 1 $$

and $Z = 13$.

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is ${}^{28}_{13}\mathrm{Al}$

Exercise 2.7.1.1

The nuclide ${}^{125}_{53}\mathrm{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$ {}^{125}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{125}_{52}\mathrm{Te} $$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$ {}^{212}_{84}\mathrm{Po} \longrightarrow {}^{208}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He} $$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\mathrm{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\mathrm{H} + {}^{97}_{42}\mathrm{Mo} \longrightarrow 2{}^{1}_{0}\mathrm{n} + {}^{97}_{43}\mathrm{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\mathrm{U} + {}_{0}{}^{1}\mathrm{n} \longrightarrow {}^{87}_{35}\mathrm{Br} + {}^{146}_{57}\mathrm{La} + 3{}^{1}_{0}\mathrm{n}$$

This page titled 2.7.1: Nuclear Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **21.2: Nuclear Equations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.7.2: Extra-Uses of Radioisotopes

Learning Objectives

By the end of this section, you will be able to:

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioimmunossays (RIA), for example, rely on radioisotopes to detect the presence and/or concentration of certain antigens. Developed by Rosalyn Sussman Yalow and Solomon Berson in the 1950s, the technique is known for extreme sensitivity, meaning that it can detect and measure very small quantities of a substance. Prior to its discovery, most similar detection relied on large enough quantities to produce visible outcomes. RIA revolutionized and expanded entire fields of study, most notably endocrinology, and is commonly used in narcotics detection, blood bank screening, early cancer screening, hormone measurement, and allergy diagnosis. Based on her significant contribution to medicine, Yalow received a Nobel Prize, making her the second woman to be awarded the prize for medicine.

Radioisotopes have revolutionized medical practice (see Appendix M), where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure **2.7.2.1**) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.



Figure **2.7.2.1**: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure **2.7.2.2**). The parent nuclide Mo-99 is part of a molybdate ion, MoO_4^{2-}; when it decays, it forms the pertechnetate ion, TcO_4^-. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.

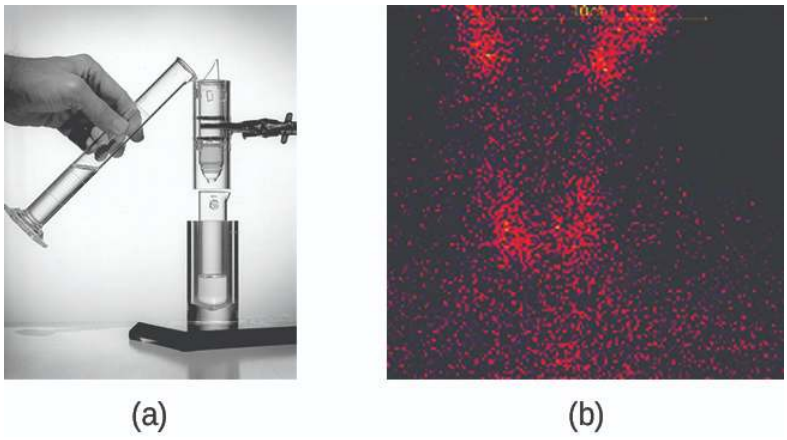


Figure **2.7.2.2**: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The is retained by the matrix in the column, whereas the passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure **2.7.2.3**). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

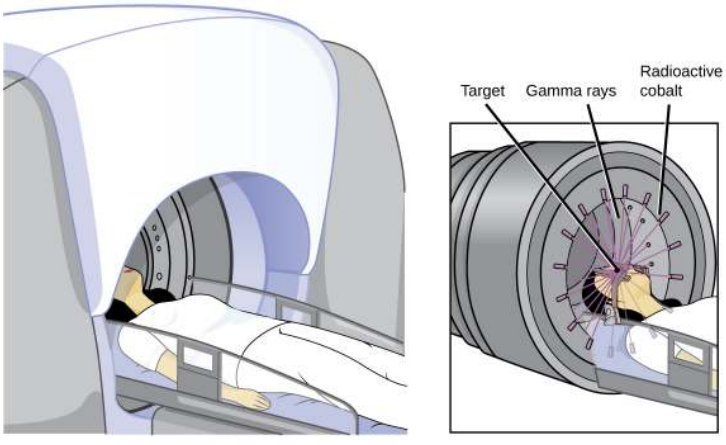


Figure **2.7.2.3**: The cartoon in (a) shows a coba machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$^{59}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma \qquad (2.7.2.1)$$

The overall decay scheme for this is shown graphically in Figure **2.7.2.4**.

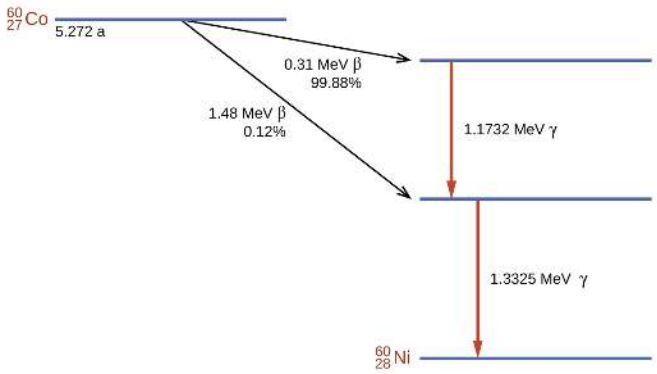


Figure **2.7.2.4**: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6CO_2(g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6O_2\ (g), \qquad (2.7.2.2)$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of ($^{14}_{6}C$). At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure **2.7.2.5**). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

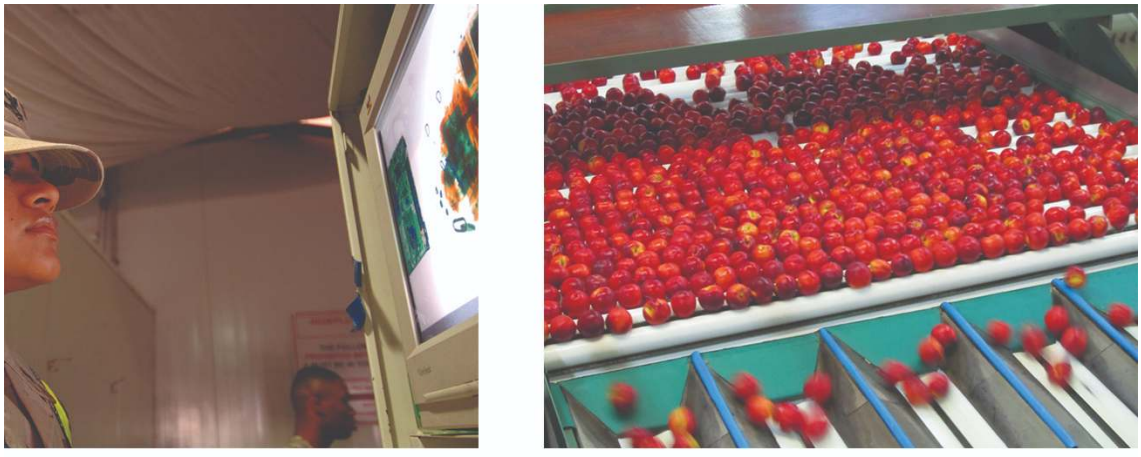


Figure **2.7.2.5**: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure **2.7.2.6**). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a

potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

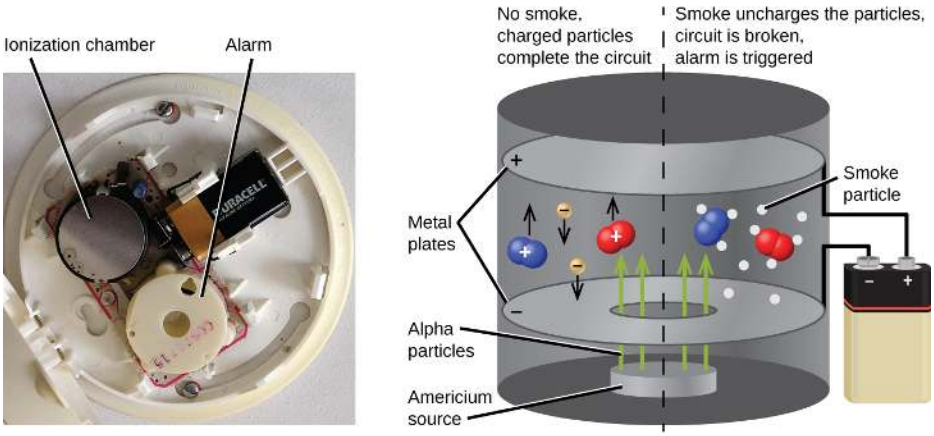


Figure **2.7.2.6**: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

This page titled 2.7.2: Extra-Uses of Radioisotopes is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **21.5: Uses of Radioisotopes** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.7.3: Extra-Biological Effects of Radiation

Learning Objectives

By the end of this section, you will be able to:

- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure **2.7.3.1**).

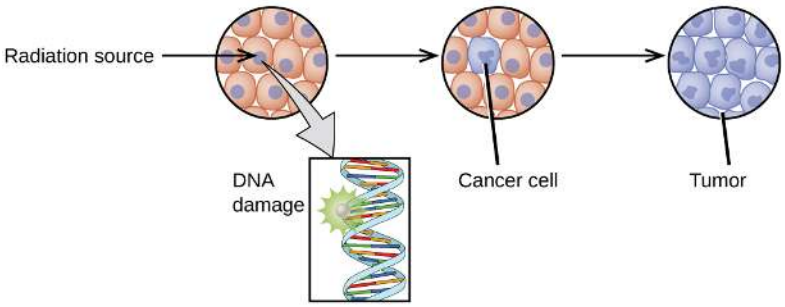


Figure **2.7.3.1**: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

2.7.3.1: Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure **2.7.3.2**).

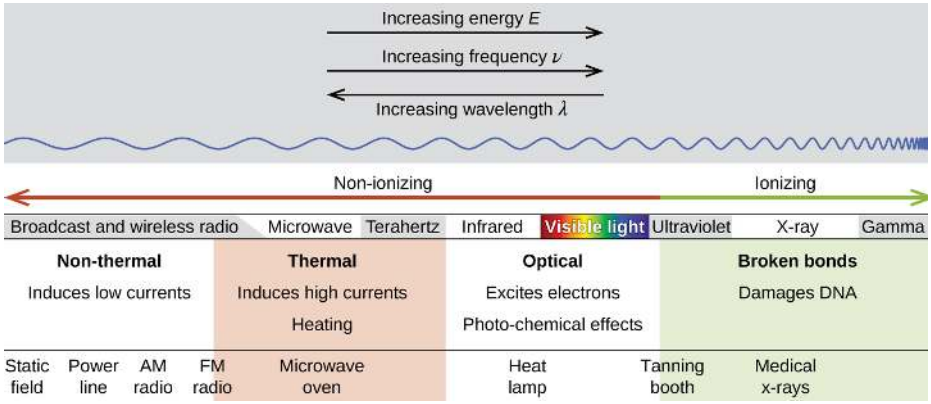


Figure **2.7.3.2**: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the

beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in Figure 21.32.

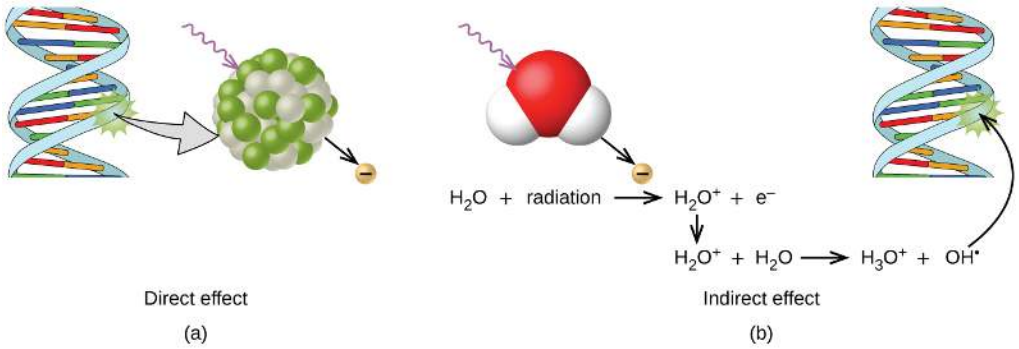


Figure 21.32 Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

2.7.3.1.1: Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure **2.7.3.3**). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

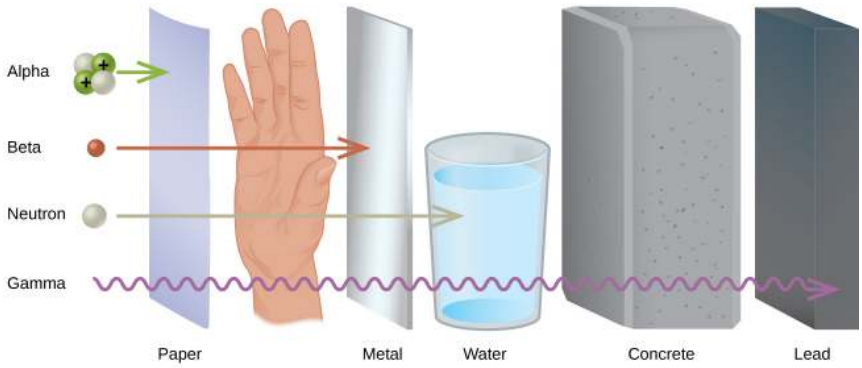


Figure **2.7.3.3**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

Chemistry in Everyday Life: Radon Exposure

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238 (Figure 21.9), which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure **2.7.3.4**).

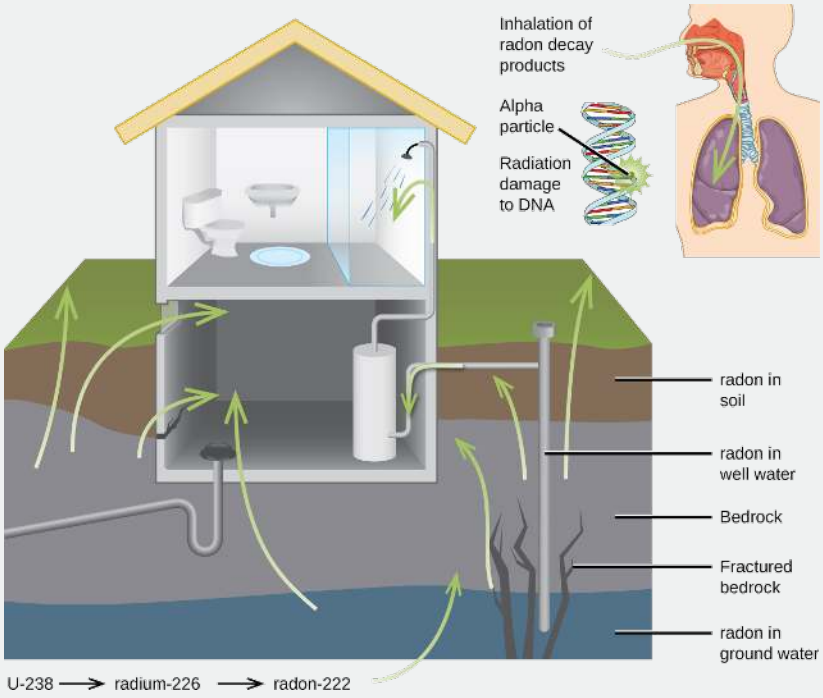


Figure **2.7.3.4**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

2.7.3.2: Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure **2.7.3.5**). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

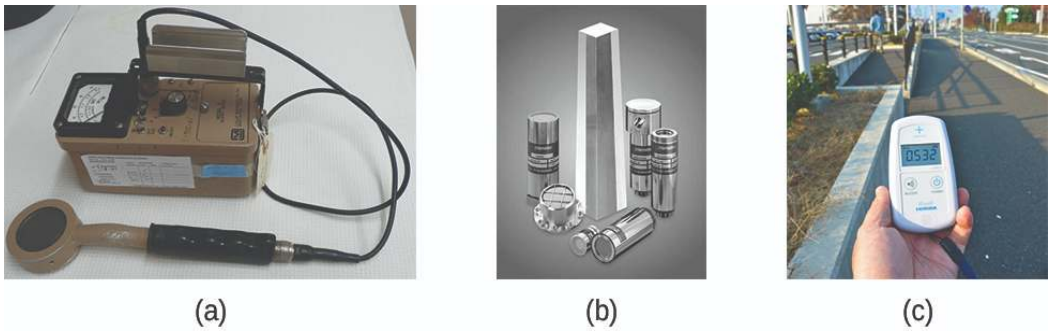


Figure **2.7.3.5**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by “osaMu”/Wikimedia commons)

A variety of units are used to measure various aspects of radiation (Figure **2.7.3.6**). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7 10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (100 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

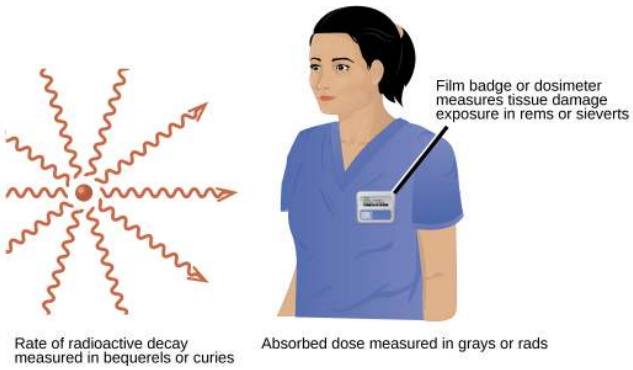


Figure **2.7.3.6**: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.

2.7.3.2.1: Units of Radiation Measurement

Table 21.4 summarizes the units used for measuring radiation.

Table 21.4: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7 10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE Gy
	roentgen equivalent for man (rem)		Rem = RBE

2.7.3.3: Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure **2.7.3.7**: , the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

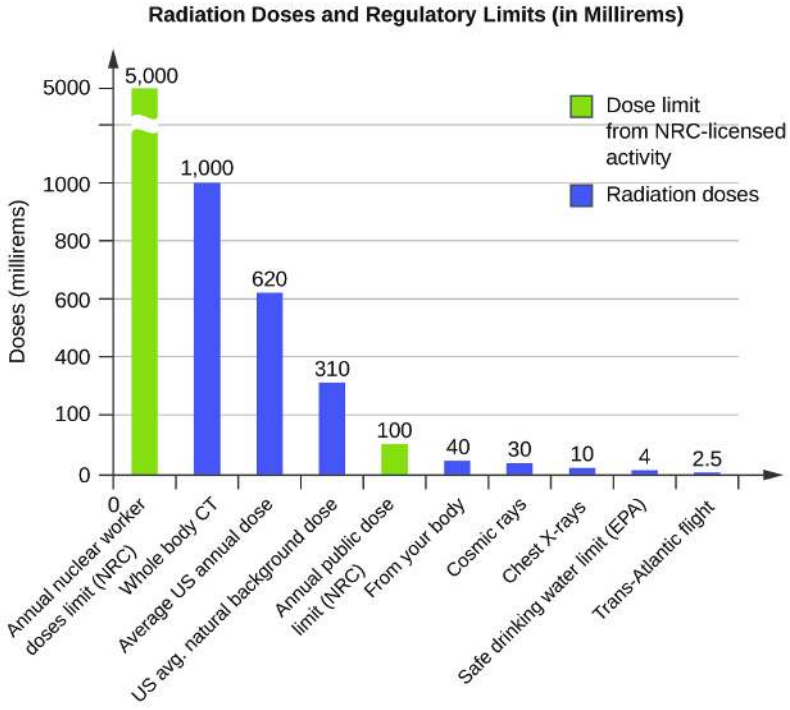


Figure **2.7.3.7**: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive

emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 21.5.

Table 21.5: Health Effects of Radiation[2]

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

2.7.3.4: Footnotes

- 2Source: US Environmental Protection Agency

This page titled 2.7.3: Extra-Biological Effects of Radiation is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **21.6: Biological Effects of Radiation** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.8: Exercises

1.

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?



2.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

3.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

4.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

5.

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

6.

How are electrons and protons similar? How are they different?

7.

How are protons and neutrons similar? How are they different?

8.

Predict and test the behavior of α particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All."

Set “Alpha Particles Energy” to “max,” and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

9.

Predict and test the behavior of α particles fired at a Rutherford atom model.

(a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the “Rutherford Atom” tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select “20” for both protons and neutrons, “min” for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to “max,” and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select “40” for both protons and neutrons, “min” for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

10.

In what way are isotopes of a given element always different? In what way(s) are they always the same?

11.

Write the symbol for each of the following ions:

(a) the ion with a 1+ charge, atomic number 55, and mass number 133

(b) the ion with 54 electrons, 53 protons, and 74 neutrons

(c) the ion with atomic number 15, mass number 31, and a 3− charge

(d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

12.

Write the symbol for each of the following ions:

(a) the ion with a 3+ charge, 28 electrons, and a mass number of 71

(b) the ion with 36 electrons, 35 protons, and 45 neutrons

(c) the ion with 86 electrons, 142 neutrons, and a 4+ charge

(d) the ion with a 2+ charge, atomic number 38, and mass number 87

13.

Open the Build an Atom simulation and click on the Atom icon.

(a) Pick any one of the first 10 elements that you would like to build and state its symbol.

(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element.
State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.

(c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.

(d) Predict whether your atom will be stable or unstable. State your reasoning.

(e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

14.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

15.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

16.

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

(a) atomic number 9, mass number 18, charge of 1−

(b) atomic number 43, mass number 99, charge of 7+

(c) atomic number 53, atomic mass number 131, charge of 1−

(d) atomic number 81, atomic mass number 201, charge of 1+

(e) Name the elements in parts (a), (b), (c), and (d).

17.

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

(a) atomic number 26, mass number 58, charge of 2+

(b) atomic number 53, mass number 127, charge of 1−

18.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_{5}\mathrm{B}$

(b) $^{199}_{80}\mathrm{Hg}$

(c) $^{63}_{29}\mathrm{Cu}$

(d) $^{13}_{6}\mathrm{C}$

(e) $^{77}_{34}\mathrm{Se}$

19.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{7}_{3}\mathrm{Li}$

(b) $^{125}_{52}\mathrm{Te}$

(c) $^{109}_{47}\mathrm{Ag}$

(d) $^{15}_{7}\mathrm{N}$

(e) $^{31}_{15}\mathrm{P}$

20.

Click on the site and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

21.

Repeat Exercise 2.20 using an element that has three naturally occurring isotopes.

22.

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

23.

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes, ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

24.

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.

25.

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.00931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

26.

The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

27.

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

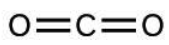
28.

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

29.

Write the molecular and empirical formulas of the following compounds:

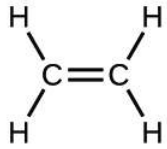
(a)



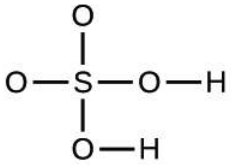
(b)



(c)



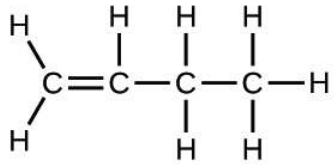
(d)



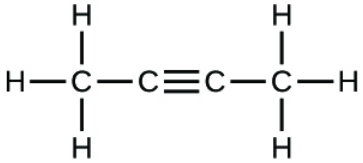
30.

Write the molecular and empirical formulas of the following compounds:

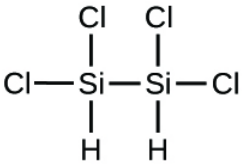
(a)



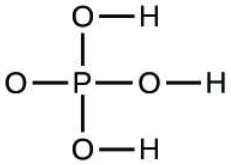
(b)



(c)



(d)



31.

Determine the empirical formulas for the following compounds:

(a) caffeine, $C_8H_{10}N_4O_2$

(b) sucrose, $C_{12}H_{22}O_{11}$

(c) hydrogen peroxide, H_2O_2

(d) glucose, $C_6H_{12}O_6$

(e) ascorbic acid (vitamin C), $C_6H_8O_6$

32.

Determine the empirical formulas for the following compounds:

(a) acetic acid, $C_2H_4O_2$

(b) citric acid, $C_6H_8O_7$

(c) hydrazine, N_2H_4

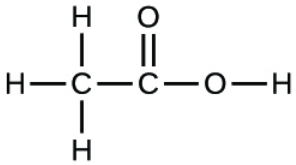
(d) nicotine, $C_{10}H_{14}N_2$

(e) butane, C_4H_{10}

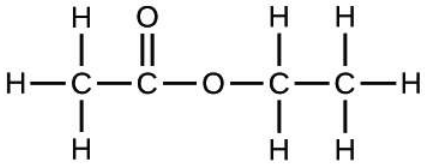
33.

Write the empirical formulas for the following compounds:

(a)



(b)



34.

Open the Build a Molecule simulation and select the “Larger Molecules” tab. Select an appropriate atom's “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound?

35.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with two carbons, six hydrogens, and one oxygen.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

36.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with three carbons, seven hydrogens, and one chlorine.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

37.

Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

38.

Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

39.

Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.

40.

Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol (C_2H_5OH), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.

41.

How are the molecular mass and the molar mass of a compound similar and how are they different?

42.

Calculate the molar mass of each of the following compounds:

(a) hydrogen fluoride, HF

(b) ammonia, NH_3

(c) nitric acid, HNO_3

(d) silver sulfate, Ag_2SO_4

(e) boric acid, $B(OH)_3$

43.

Calculate the molar mass of each of the following:

(a) S_8

(b) C_5H_{12}

(c) $Sc_2(SO_4)_3$

(d) CH_3COCH_3 (acetone)

(e) $C_6H_{12}O_6$ (glucose)

44.

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

(a) limestone, $CaCO_3$

(b) halite, NaCl

(c) beryl, $Be_3Al_2Si_6O_{18}$

(d) malachite, $Cu_2(OH)_2CO_3$

(e) turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

45.

Calculate the molar mass of each of the following:

(a) the anesthetic halothane, $C_2HBrClF_3$

(b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$

(c) caffeine, $C_8H_{10}N_4O_2$

(d) urea, $CO(NH_2)_2$

(e) a typical soap, $C_{17}H_{35}CO_2Na$

46.

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

47.

Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) 1.6×10^{-3} mol $Na_2 SO_4$

(d) 6.854×10^3 mol glucose, $C_6 H_{12} O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

48.

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

(a) 2.12 g of potassium bromide, KBr

(b) 0.1488 g of phosphoric acid, H_3PO_4

(c) 23 kg of calcium carbonate, $CaCO_3$

(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$

(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

49.

Determine the mass of each of the following:

(a) 2.345 mol LiCl

(b) 0.0872 mol acetylene, C_2H_2

(c) 3.3×10^{-2} mol $Na_2 CO_3$

(d) 1.23×10^3 mol fructose, $C_6 H_{12} O_6$

(e) 0.5758 mol $FeSO_4(H_2O)_7$

50.

The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?

51.

Determine the mass in grams of each of the following:

(a) 0.600 mol of oxygen atoms

(b) 0.600 mol of oxygen molecules, O_2

(c) 0.600 mol of ozone molecules, O_3

52.

A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

53.

Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, $ZrSiO_4$, a semiprecious stone.

54.

Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4, 0.6 mol of C_6H_6, or 0.4 mol of C_3H_8.

55.

Determine which of the following contains the greatest mass of aluminum: 122 g of $AlPO_4$, 266 g of Al_2Cl_6, or 225 g of Al_2S_3.

56.

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

57.

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

58.

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

59.

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

60.

A tube of toothpaste contains 0.76 g of sodium monofluorophosphate (Na_2PO_3F) in 100 mL.

(a) What mass of fluorine atoms in mg was present?

(b) How many fluorine atoms were present?

61.

Which of the following represents the least number of molecules?

(a) 20.0 g of H_2O (18.02 g/mol)

(b) 77.0 g of CH_4 (16.06 g/mol)

(c) 68.0 g of C_3H_6 (42.08 g/mol)

(d) 100.0 g of N_2O (44.02 g/mol)

(e) 84.0 g of HF (20.01 g/mol)

This page titled 2.8: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

2.8.1: Answers to Selected Exercises

1.

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

3.

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

5.

Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

7.

Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

9.

(a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

11.

(a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

13.

(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

15.

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or $_{3}^{6}\mathbf{Li}$. (b) $^{6}Li^{+}$ or msubsupmsubsupmsupmsup

17.

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

19.

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

21.

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of

Ne-21. The average mass would be 20.18 amu. Checking the nature's mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

23.

79.90 amu

25.

Turkey source: 20.3% (of 10.0129 amu isotope); US source: 19.1% (of 10.0129 amu isotope)

27.

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

29.

(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

31.

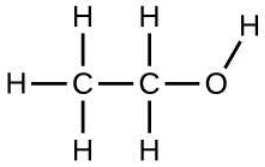
(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

33.

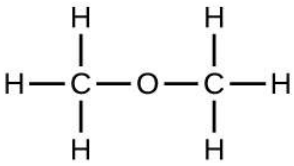
(a) CH_2O; (b) C_2H_4O

35.

(a) ethanol



(b) methoxymethane, more commonly known as dimethyl ether



(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

37.

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

39.

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

41.

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

43.

(a) 256.48 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}

45.

(a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}

47.

(a) 0.819 g;
(b) 307 g;
(c) 0.23 g;
(d) 1.235×10^6 g (1235 kg);
(e) 765 g

49.

(a) 99.41 g;
(b) 2.27 g;
(c) 3.5 g;
(d) 222 kg;
(e) 160.1 g

51.

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

53.

zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g

55.

$AlPO_4$: 1.000 mol or 26.98 g Al
Al_2Cl_6: 1.994 mol or 53.74 g Al
Al_2S_3: 3.00 mol or 80.94 g Al
The Al_2S_3 sample thus contains the greatest mass of Al.

57.

3.113×10^{25} C atoms

59.

0.865 servings, or about 1 serving.

61.

20.0 g H_2O represents the least number of molecules since it has the least number of moles.

This page titled 2.8.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

2.9: Exercises for Nuclear Reactions

1. Write the following isotopes in hyphenated form (e.g., “carbon-14”)

(a) $^{24}_{11}\mathrm{Na}$
(b) $^{29}_{13}\mathrm{Al}$
(c) $^{73}_{36}\mathrm{Kr}$
(d) $^{194}_{77}\mathrm{Ir}$

2. Write the following isotopes in nuclide notation (e.g.,

a. oxygen-14
b. copper-70
c. tantalum-175
d. francium-217

3. For the following isotopes that have missing information, fill in the missing information to complete the notation

(a) $^{34}_{14}\mathrm{X}$
(b) $^{36}_{X}\mathrm{P}$
(c) $^{57}_{X}\mathrm{Mn}$
(d) $^{121}_{56}\mathrm{X}$

4. For each of the isotopes in Exercise 21.1, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

a. 25 protons, 20 neutrons, 24 electrons
b. 45 protons, 24 neutrons, 43 electrons
c. 53 protons, 89 neutrons, 54 electrons
d. 97 protons, 146 neutrons, 97 electrons

6. Calculate the density of the nucleus in g/mL, assuming that it has the typical nuclear diameter of 1 10^{-13} cm and is spherical in shape. 7. What are the two principal differences between nuclear reactions and ordinary chemical changes?

8. The mass of the atom is 22.9898 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

9. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

a. chlorine-37
b. calcium-40
c. $^{204}\mathrm{Bi}$
d. $^{56}\mathrm{Fe}$
e. $^{206}\mathrm{Pb}$
f. $^{211}\mathrm{Pb}$
g. $^{222}\mathrm{Rn}$
h. carbon-14

10. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

a. argon-40
b. oxygen-16
c. $^{122}\mathrm{Ba}$
d. $^{58}\mathrm{Ni}$
e. $^{205}\mathrm{Tl}$

f. ^{210}Tl
g. ^{226}Ra
h. magnesium-24

11. Write a brief description or definition of each of the following:

a. nucleon
b. α particle
c. β particle
d. positron
e. γ ray
f. nuclide
g. mass number
h. atomic number

12. Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

13. Complete each of the following equations by adding the missing species:

(a) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow \text{?} + {}^{1}_{0}\text{n}$
(b) $^{239}_{94}\text{Pu} + \text{?} \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
(c) $^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow \text{?} + {}^{1}_{1}\text{H}$
(d) $^{235}_{92}\text{U} \rightarrow \text{?} + {}^{135}_{55}\text{Cs} + 4{}^{1}_{0}\text{n}$

14. Complete each of the following equations:

(a) $^{7}_{3}\text{Li} + \text{?} \rightarrow 2{}^{4}_{2}\text{He}$
(b) $^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + \text{?}$
(c) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow \text{?} + {}^{1}_{0}\text{n}$
(d) $^{250}_{96}\text{Cm} \rightarrow \text{?} + {}^{98}_{38}\text{Sr} + 4{}^{1}_{0}\text{n}$

15. Write a balanced equation for each of the following nuclear reactions:

a. the production of ^{17}O from ^{14}N by α particle bombardment
b. the production of ^{14}C from ^{14}N by neutron bombardment
c. the production of ^{233}Th from ^{232}Th by neutron bombardment
d. the production of ^{239}U from ^{238}U by bombardment

16. Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as ^{99}Tc*. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

17. The mass of the atom is 18.99840 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

18. For the reaction if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273K and 1 atm?

19. What are the types of radiation emitted by the nuclei of radioactive elements?

20. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

a. an α particle is emitted
b. a β particle is emitted
c. γ radiation is emitted
d. a positron is emitted
e. an electron is captured

21. What is the change in the nucleus that results from the following decay scenarios?

a. emission of a β particle
b. emission of a β^+ particle
c. capture of an electron

22. Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

23. Why is electron capture accompanied by the emission of an X-ray?

24. Explain, in terms of Figure 21.2, how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

25. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

a. chromium-53
b. manganese-51
c. iron-59

26. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

(a) $^{34}_{15}\mathrm{P}$
(b) $^{239}_{92}U$
(c) $^{38}_{20}\mathrm{Ca}$
(d) $^{3}_{1}\mathrm{H}$
(e) $^{245}_{94}\mathrm{Pu}$

27. The following nuclei do not lie in the band of stability. How would they be expected to decay?

(a) $^{28}_{15}\mathrm{P}$
(b) $^{235}_{92}\mathrm{U}$
(c) $^{37}_{20}\mathrm{Ca}$
(d) $^{9}_{3}\mathrm{Li}$
(e) $^{245}_{96}\mathrm{Cm}$

28. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

(a) $^{6}_{2}\mathrm{He}$
(b) $^{60}_{30}\mathrm{Zn}$
(c) $^{235}_{91}\ \mathrm{Pa}$
(d) $^{241}_{94}\ \mathrm{Np}$
(e) $^{18}\ \mathrm{F}$
(f) $^{129}\mathrm{Ba}$
(g) $^{237}\mathrm{Pu}$

29. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α particles, in that order.

30. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

31. Define the term half-life and illustrate it with an example.

32. A 1.00 10^{-6}-g sample of nobelium, has a half-life of 55 seconds after it is formed. What is the percentage of remaining at the following times?

a. 5.0 min after it forms
b. 1.0 h after it forms

33. ^{239}Pu is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ^{239}Pu present today will be present in 1000 y?

34. The isotope ^{208}Tl undergoes β decay with a half-life of 3.1 min.

a. What isotope is produced by the decay?
b. How long will it take for 99.0% of a sample of pure ^{208}Tl to decay?
c. What percentage of a sample of pure ^{208}Tl remains un-decayed after 1.0 h?

35. If 1.000 g of produces 0.0001 mL of the gas at STP (standard temperature and pressure) in 24 h, what is the half-life of ^{226}Ra in years?

36. The isotope is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

37. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of

38. What is the age of mummified primate skin that contains 8.25% of the original quantity of ^{14}C?

39. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

a. Calculate the age of the rock if the half-life of the decay of rubidium by β emission is $4.7\ 10^{10}$ y.
b. If some was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

40. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of and 2.52 mg of Calculate the age of the ore. The half-life of is $4.5\ 10^{9}$ yr.

41. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed $4.7\ 10^{9}$ years ago?

42. A atom (mass = 7.0169 amu) decays into a atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

43. A atom (mass = 8.0246 amu) decays into a atom (mass = 8.0053 amu) by loss of a β^+ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

44. Isotopes such as ^{26}Al (half-life: $7.2\ 10^{5}$ years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

a. ^{26}Al decays by β^+ emission or electron capture. Write the equations for these two nuclear transformations.
b. The earth was formed about $4.7\ 10^{9}$ (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

45. Write a balanced equation for each of the following nuclear reactions:

a. bismuth-212 decays into polonium-212
b. beryllium-8 and a positron are produced by the decay of an unstable nucleus
c. neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
d. strontium-90 decays into yttrium-90

46. Write a balanced equation for each of the following nuclear reactions:

a. mercury-180 decays into platinum-176
b. zirconium-90 and an electron are produced by the decay of an unstable nucleus
c. thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
d. neon-19 decays into fluorine-19

47. Write the balanced nuclear equation for the production of the following transuranium elements:

a. berkelium-244, made by the reaction of Am-241 and He-4
b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
c. lawrencium-257, made by the reaction of Cf-250 and B-11
d. dubnium-260, made by the reaction of Cf-249 and N-15

48. How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

49. Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

50.Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

51. Describe the components of a nuclear reactor.

52. In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

53. Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

54. The mass of a hydrogen atom is 1.007825 amu; that of a tritium atom is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of produced is released by the following fusion reaction:

55. How can a radioactive nuclide be used to show that the equilibrium is a dynamic equilibrium?

56. Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

57. Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-133 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

a. Write an equation for the decay.
b. How long will it take for 95.0% of a dose of I-131 to decay?

58. If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

a. cobalt-60 (a strong γ emitter used for irradiation)
b. molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

59. Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

60. Given specimens uranium-232 ($t_{1/2}$ = 68.9 y) and uranium-233 ($t_{1/2}$ = 159,200 y) of equal mass, which one would have greater activity and why?

61. A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

a. What is its activity in Bq?
b. What is its activity in Ci?

62. Given specimens neon-24 ($t_{1/2}$ = 3.38 min) and bismuth-211 ($t_{1/2}$ = 2.14 min) of equal mass, which one would have greater activity and why?

This page titled 2.9: Exercises for Nuclear Reactions is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **21.10: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.9.1: Answers to Exercises for Nuclear Reactions

1.

(a) sodium-24; (b) aluminum-29; (c) krypton-73; (d) iridium-194

3.

(a) msubsupmsubsupSi; (b) msubsupmsubsupP; (c) msubsupmsubsupMn; (d) msubsup

5.

(a) msubsupmsubsupmsupmsup; (b) msubsupmsubsupmsupmsup; (c) msubsupmsubsupmsupmsup; (d) msubsup

7.

Nuclear reactions usually change one type of nucleus into another; chemical changes rearrange atoms. Nuclear reactions involve much larger energies than chemical reactions and have measureable mass changes.

9.

(a), (b), (c), (d), and (e)

11.

(a) A nucleon is any particle contained in the nucleus of the atom, so it can refer to protons and neutrons. (b) An α particle is one product of natural radioactivity and is the nucleus of a helium atom. (c) A β particle is a product of natural radioactivity and is a high-speed electron. (d) A positron is a particle with the same mass as an electron but with a positive charge. (e) Gamma rays compose electromagnetic radiation of high energy and short wavelength. (f) Nuclide is a term used when referring to a single type of nucleus. (g) The mass number is the sum of the number of protons and the number of neutrons in an element. (h) The atomic number is the number of protons in the nucleus of an element.

13.

(a) msubsupmsubsupAl + msubsupmsubsupHe $\longrightarrow$ $^{30}_{15}\mathrm{P}$ + msubsupmsubsupn; (b) msubsupmsubsupPu + msubsupmsubsupHe $\longrightarrow$ $^{242}_{96}\mathrm{Cm}$ + msubsupmsubsupn; (c) msubsupmsubsupN + msubsupmsubsupHe $\longrightarrow$ $^{17}_{8}\mathrm{O}$ + msubsupmsubsupH; (d) msubsupmsubsupU $\longrightarrow$ $^{96}_{37}\mathrm{Rb}$ + msubsupmsubsupCs+

15.

(a) msubsupmsubsupN + msubsupmsubsupHe $\longrightarrow$ msubsupmsubsupO + msubsupmsubsupH; (b) msubsupmsubsupC + msubsupmsubsupn $\longrightarrow$ msubsupmsubsupC + msubsupmsubsupH; (c) msubsupmsubsupTh + msubsupmsubsupn $\longrightarrow$ msubsupmsubsupTh; (d) msubsupmsubsupU + msubsupmsubsupH $\longrightarrow$ msubsupmsubsupU + msubsupmsubsupH

17.

(a) 148.8 MeV per atom; (b) 7.808 MeV/nucleon

19.

α (helium nuclei), β (electrons), β^+ (positrons), and η (neutrons) may be emitted from a radioactive element, all of which are particles; γ rays also may be emitted.

21.

(a) conversion of a neutron to a proton: msubsupmsubsupn $\longrightarrow$ msubsupmsubsupp + msubsupmsubsupe; (b) conversion of a proton to a neutron; the positron has the same mass as an electron and the same magnitude of positive charge as the electron has negative charge; when the n:p ratio of a nucleus is too low, a proton is converted into a neutron with the emission of a positron: msubsupmsubsupp $\longrightarrow$ msubsupmsubsupn + msubsupmsubsupe; (c) In a proton-rich nucleus, an inner atomic electron can be absorbed. In simplest form, this changes a proton into a neutron: msubsupmsubsupp + msubsupmsubsupe $\longrightarrow$ msubsupmsubsupp

23.

The electron pulled into the nucleus was most likely found in the 1*s* orbital. As an electron falls from a higher energy level to replace it, the difference in the energy of the replacement electron in its two energy levels is given off as an X-ray.

25.

Manganese-51 is most likely to decay by positron emission. The n:p ratio for Cr-53 is $\frac{29}{24}$ = 1.21; for Mn-51, it is $\frac{26}{25}$ = 1.04; for Fe-59, it is $\frac{33}{26}$ = 1.27. Positron decay occurs when the n:p ratio is low. Mn-51 has the lowest n:p ratio and therefore is most likely to decay by positron emission. Besides, msubsupmsubsupCr is a stable isotope, and msubsupmsubsupFe decays by beta emission.

27.

(a) positron emission; (b) α decay; (c) positron emission; (d) β decay; (e) α decay

29.

msubsupmsubsupU ⟶ msubsupmsubsupTh + msubsupmsubsupHe;
msubsupmsubsupPa ⟶ msubsupmsubsupU + msubsupmsubsupe;
msubsupmsubsupTh ⟶ msubsupmsubsupRa + msubsupmsubsupHe
msubsupmsubsupRn ⟶ msubsupmsubsupPo + msubsupmsubsupHe
msubsupmsubsupTh ⟶ msubsupmsubsupPa + msubsupmsubsupe;
msubsupmsubsupU ⟶ msubsupmsubsupTh + msubsupmsubsupHe
msubsupmsubsupRa ⟶ msubsupmsubsupRn + msubsupmsubsupHe;

31.

Half-life is the time required for half the atoms in a sample to decay. Example (answers may vary): For C-14, the half-life is 5770 years. A 10-g sample of C-14 would contain 5 g of C-14 after 5770 years; a 0.20-g sample of C-14 would contain 0.10 g after 5770 years.

33.

$\left(\frac{1}{2}\right)^{0.04} = 0.973$ or 97.3%

35.

2×10^3 y

37.

0.12 h^{-1}

39.

(a) 3.8 billion years; (b) The rock would be younger than the age calculated in part (a). If Sr was originally in the rock, the amount produced by radioactive decay would equal the present amount minus the initial amount. As this amount would be smaller than the amount used to calculate the age of the rock and the age is proportional to the amount of Sr, the rock would be younger.

41.

c = 0; This shows that no Pu-239 could remain since the formation of the earth. Consequently, the plutonium now present could not have been formed with the uranium.

43.

17.5 MeV

45.

(a) msubsupmsubsupBi ⟶ msubsupmsubsupPo + msubsupmsubsupe; (b) msubsupmsubsupB ⟶ msubsupmsubsupBe + msubsupmsubsupe; (c) msubsupmsubsupU + msubsupmsubsupn ⟶ msubsupmsubsupNp + msubsupmsubsupNp, msubsupmsubsupNp ⟶ msubsupmsubsupPu + msubsupmsubsupe; (d) msubsupmsubsupSr ⟶ msubsupmsubsupY + msubsupmsubsupe

47.

(a) msubsupmsubsupAm + msubsupmsubsupHe ⟶ msubsupmsubsupBk + msubsupmsubsupn; (b) msubsupmsubsupPu + 15msubsupmsubsupn ⟶ msubsupmsubsupFm + 6msubsupmsubsupe; (c) msubsupmsubsupCf + msubsupmsubsupB ⟶ msubsupmsubsupLr + 4msubsupmsubsupn; (d) msubsupmsubsupCf + msubsupmsubsupN ⟶ msubsupmsubsupDb + 4msubsup

49.

Two nuclei must collide for fusion to occur. High temperatures are required to give the nuclei enough kinetic energy to overcome the very strong repulsion resulting from their positive charges.

51.

A nuclear reactor consists of the following:

1. A nuclear fuel. A fissionable isotope must be present in large enough quantities to sustain a controlled chain reaction. The radioactive isotope is contained in tubes called fuel rods.
2. A moderator. A moderator slows neutrons produced by nuclear reactions so that they can be absorbed by the fuel and cause additional nuclear reactions.
3. A coolant. The coolant carries heat from the fission reaction to an external boiler and turbine where it is transformed into electricity.
4. A control system. The control system consists of control rods placed between fuel rods to absorb neutrons and is used to adjust the number of neutrons and keep the rate of the chain reaction at a safe level.
5. A shield and containment system. The function of this component is to protect workers from radiation produced by the nuclear reactions and to withstand the high pressures resulting from high-temperature reactions.

53.

The fission of uranium generates heat, which is carried to an external steam generator (boiler). The resulting steam turns a turbine that powers an electrical generator.

55.

Introduction of either radioactive Ag^+ or radioactive Cl^- into the solution containing the stated reaction, with subsequent time given for equilibration, will produce a radioactive precipitate that was originally devoid of radiation.

57.

(a) $^{133}_{53}\text{I} \longrightarrow {}^{133}_{54}\text{Xe} + {}^{0}_{-1}\text{e}$; (b) 37.6 days

59.

Alpha particles can be stopped by very thin shielding but have much stronger ionizing potential than beta particles, X-rays, and γ-rays. When inhaled, there is no protective skin covering the cells of the lungs, making it possible to damage the DNA in those cells and cause cancer.

61.

(a) 7.64×10^9 Bq; (b) 2.06×10^{-2} Ci

This page titled 2.9.1: Answers to Exercises for Nuclear Reactions is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

3: Ions, Compounds, and Molecules

3.1: Molecular and Ionic Compounds

3.2: Chemical Nomenclature

3.3: Electronic Structure of Atoms (Electron Configurations)

3.3.1: Extra-Orbital Origin and Shape

3.4: Ionic Bonding

3.5: Covalent Bonding

3.6: Exercises

3.6.1: Answers to Selected Exercises

This page titled 3: Ions, Compounds, and Molecules is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

3.1: Molecular and Ionic Compounds

Learning Objectives

By the end of this section, you will be able to:

- 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 **3.1.1**).

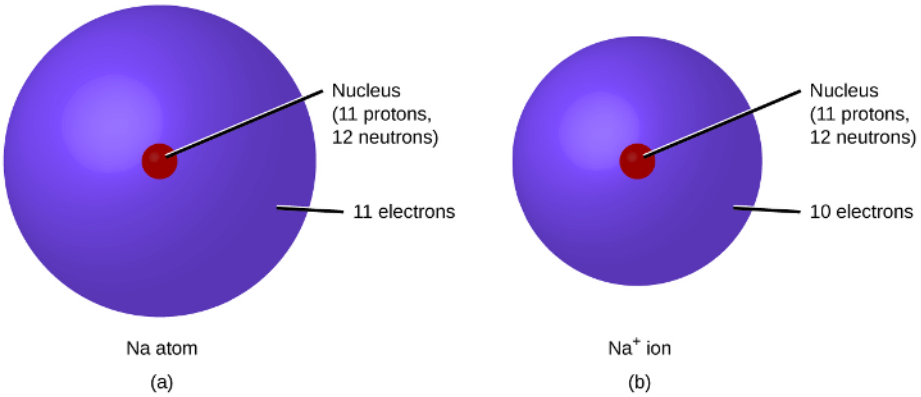


Table **3.1.1**: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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 **3.1.2**). 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.

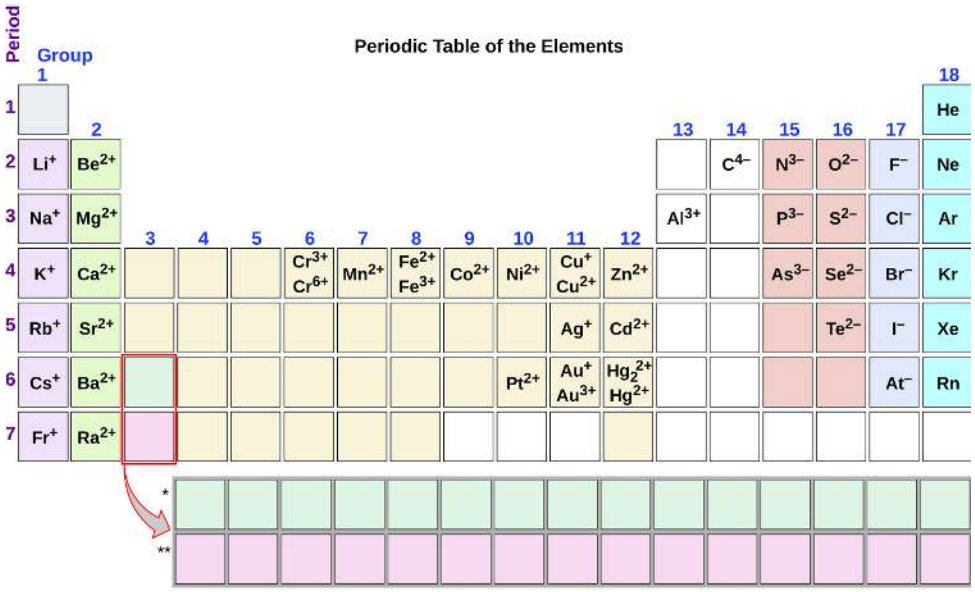


Table **3.1.2**: Some elements exhibit a regular pattern of ionic charge when they form ions.

✔ Example 3.1.1: 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 3.1.1

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

Answer

Se^{2-}, the selenide ion

✔ Example 3.1.2: 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 3.1.2

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 **3.1.1**. 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 **3.1.1**: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O		
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_{42}^-	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.

3.1.1: 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 **3.1.3**).

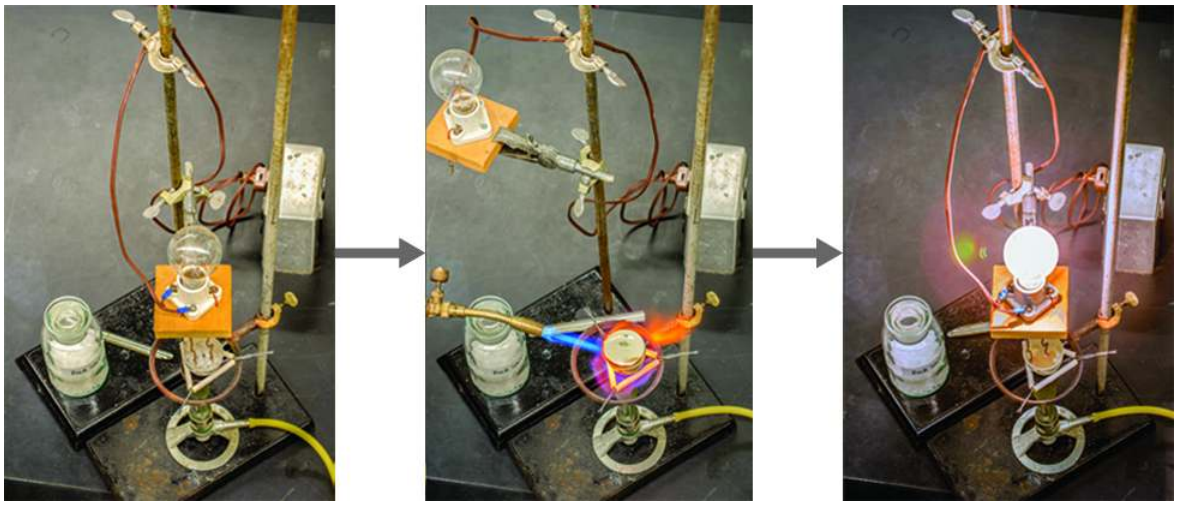


Table **3.1.3**: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Link to Learning

Watch this video to see a mixture of salts melt and conduct electricity.

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 3.1.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure **3.1.4**) 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?



Table **3.1.4**: 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 via Wikipedia)

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 3.1.3

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 **3.1.1**) 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 $\mathbf{Ca_3(PO_4)_2}$. This formula indicates that there are three calcium ions ($\mathbf{Ca^{2+}}$) 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 3.1.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions $\mathbf{Ca^{2+}}$ 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 3.1.4

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, $C_2O_4^{2-}$.

3.1.2: 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 3.1.5: 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 3.1.5

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
b. ionic

c. molecular
d. ionic

This page titled 3.1: Molecular and Ionic Compounds is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.6: Molecular and Ionic Compounds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.2: Chemical Nomenclature

Learning Objectives

By the end of this section, you will be able to:

- 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.

3.2.1: 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.

3.2.2: 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 **3.2.1**.

Table **3.2.1**: 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

3.2.3: Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in Table **3.2.2**.

Table **3.2.2**: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	NH_4Cl, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Chemistry in Everyday Life: Ionic Compounds in Your Cabinet

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 **3.2.3**. 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 **3.2.3**: Everyday Ionic Compounds

Ionic Compound	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 as antacid)
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

3.2.4: Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group 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+ (see Figure 2.29), 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 **3.2.4**.

Table **3.2.4**: Some Ionic Compounds with Variably Charged Metal Ions

Compound	Name
$FeCl_2$	iron(II) chloride
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
SnF_2	tin(II) fluoride
SnF_4	tin(IV) fluoride

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.

3.2.5: Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the anhydrous (meaning "not hydrated") compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see Table **3.2.5**) and ends with "hydrate." For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water. The two examples mentioned in the previous paragraph are represented by the formulas

$$\textbf{copper(II) sulfate pentahydrate} \quad CuSO_4 \cdot 5H_2O$$

$$\textbf{sodium carbonate decahydrate} \quad Na_2CO_3 \cdot 10H_2O$$

Table **3.2.5**: 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-

Example **3.2.1**: Naming Ionic Compounds

Name the following ionic compounds

a. Fe_2S_3
b. CuSe
c. GaN
d. $MgSO_4 \cdot 7H_2O$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, and 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+}, Mg^{2+}, 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. magnesium sulfate heptahydrate
e. titanium(III) sulfate

Exercise 3.2.1

Write the formulas of the following ionic compounds:

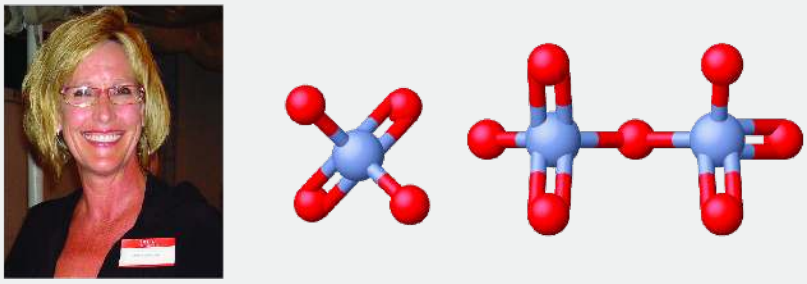
a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. iron(III) chloride dihydrate

Answer

(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) $FeCl_3 \cdot 2H_2O$

Chemistry in Everyday Life: Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure **3.2.1**) 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 Brockovich* (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 **3.2.1**: (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, (left), and dichromate, (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. But Cr(VI) 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.

3.2.6: 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.

3.2.7: 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 **3.2.5**.

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 **3.2.6**.

Table **3.2.6**: 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	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide	P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide	IF_7	iodine 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 **3.2.2**: 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 **3.2.2**

Write the formulas for the following compounds:

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

Answer

(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

Link to Learning

The following website provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

3.2.8: 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 **3.2.7**.

Table **3.2.7**: 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

3.2.9: 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 **3.2.8**. 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 **3.2.8**: 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

This page titled 3.2: Chemical Nomenclature is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **2.7: Chemical Nomenclature** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.3: Electronic Structure of Atoms (Electron Configurations)

Learning Objectives

By the end of this section, you will be able to:

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

3.3.1: Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure **3.3.1**: depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

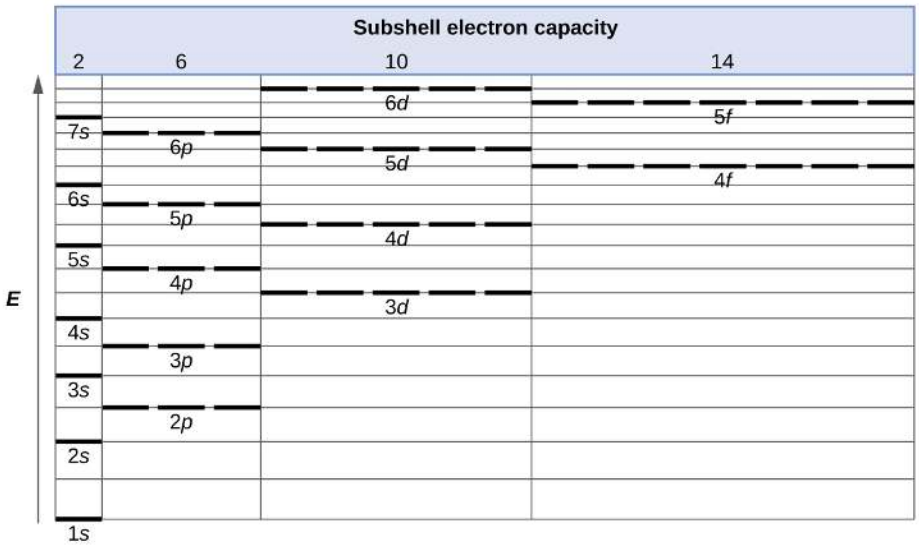


Figure **3.3.1**: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, n, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of l increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have $+Z$ charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to n is more

significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure **3.3.2**):

1. The number of the principal quantum shell, n,
2. The letter that designates the orbital type (the subshell, l), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

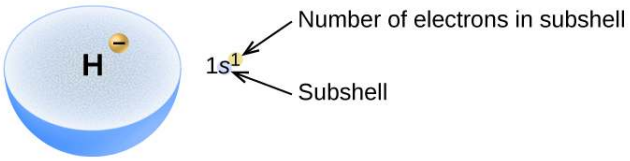


Figure **3.3.2**: The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

3.3.2: The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure **3.3.1**), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure **3.3.3** illustrates the traditional way to remember the filling order for atomic orbitals.

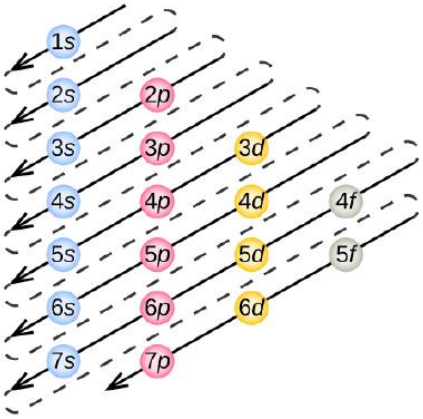


Figure **3.3.3**: This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, Figure **3.3.4** provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

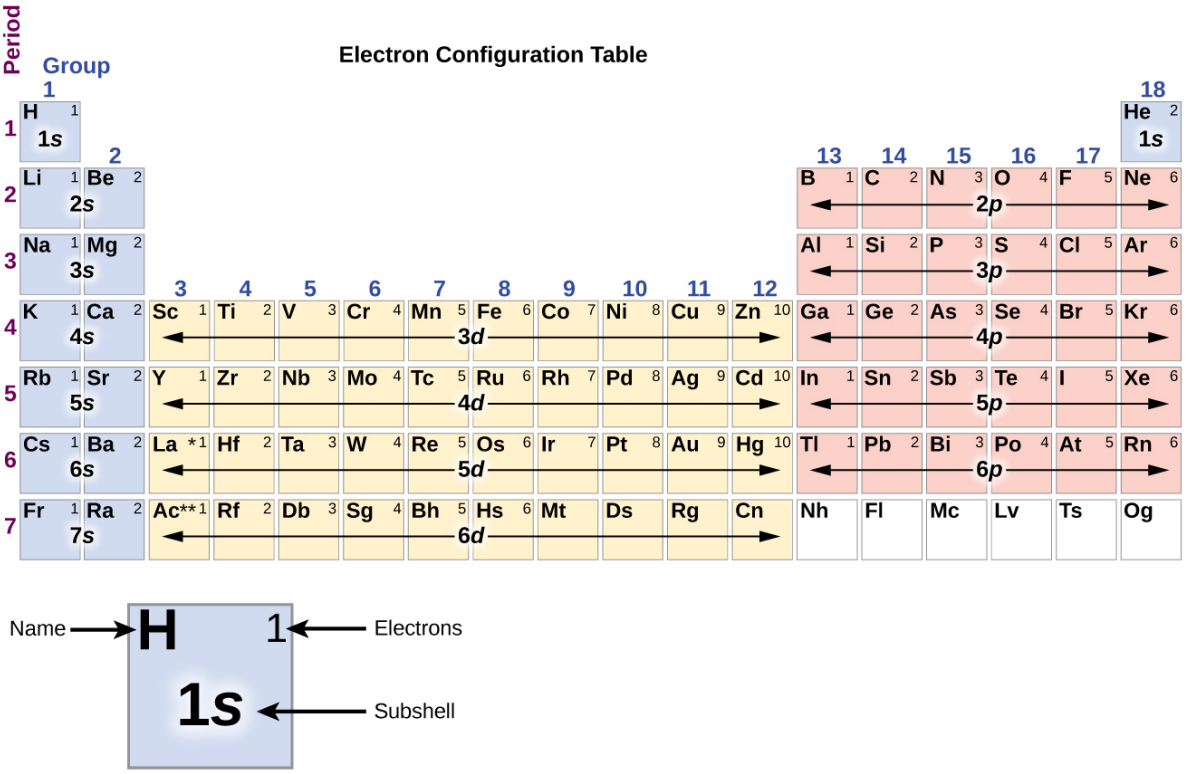
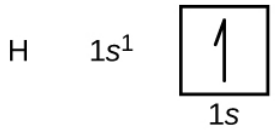
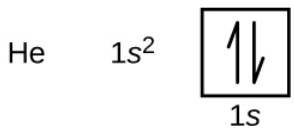


Figure **3.3.4**: This partial periodic table shows electron configurations for the valence subshells of atoms. By "building up" from hydrogen, this table can be used to determine the electron configuration for atoms of most elements in the periodic table. (Electron configurations of the lanthanides and actinides are not accurately predicted by this simple approach. See Figure **3.3.6**:

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure **3.3.3** or Figure **3.3.4**, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (\(*n* = 1\), \(*l* = 0\), \(*m*_*l* = 0\), $m_s = +\frac{1}{2}$. The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and ml quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

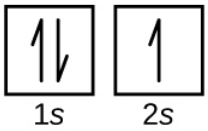


The $n = 1$ shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next

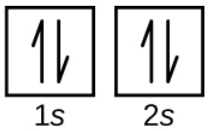
lowest energy, the 2*s* orbital (Figure **3.3.3** or Figure **3.3.4**). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



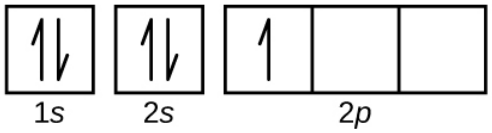
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



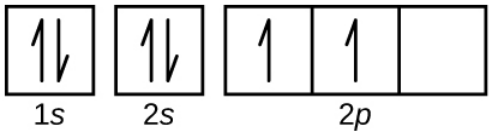
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals ($m_l = -1, 0, +1$) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

B $1s^2 2s^2 2p^1$

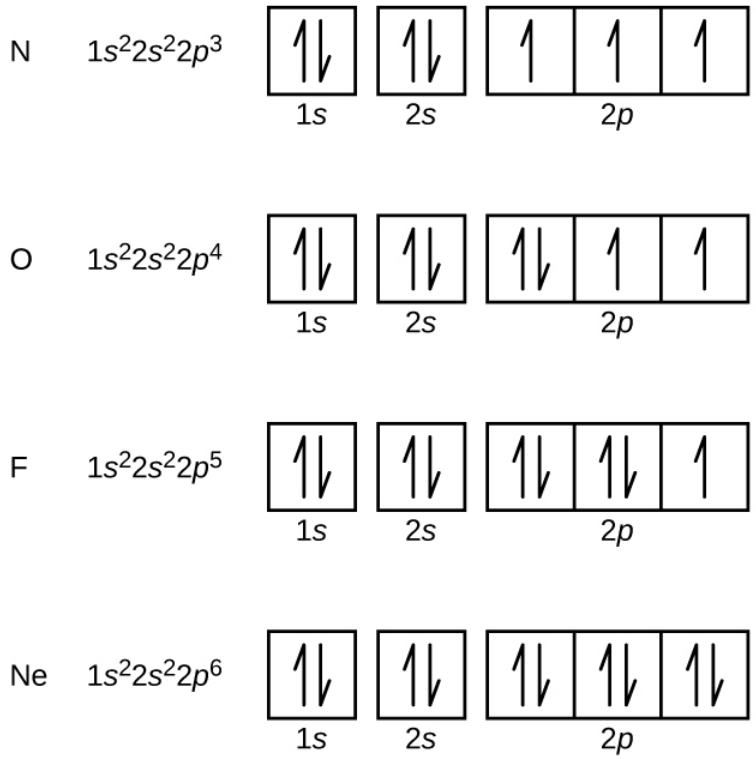


Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

C $1s^2 2s^2 2p^2$



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure **3.3.5**). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

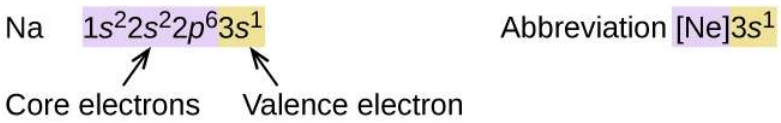


Figure **3.3.5**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$Li : [He]2s^1$$
$$Na : [Ne]3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[Ne]3s^2$ configuration, is analogous to its family member beryllium, $[He]2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[Ne]3s^2 3p^1$, is analogous to its family member boron, $[He]2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure **3.3.6**: shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

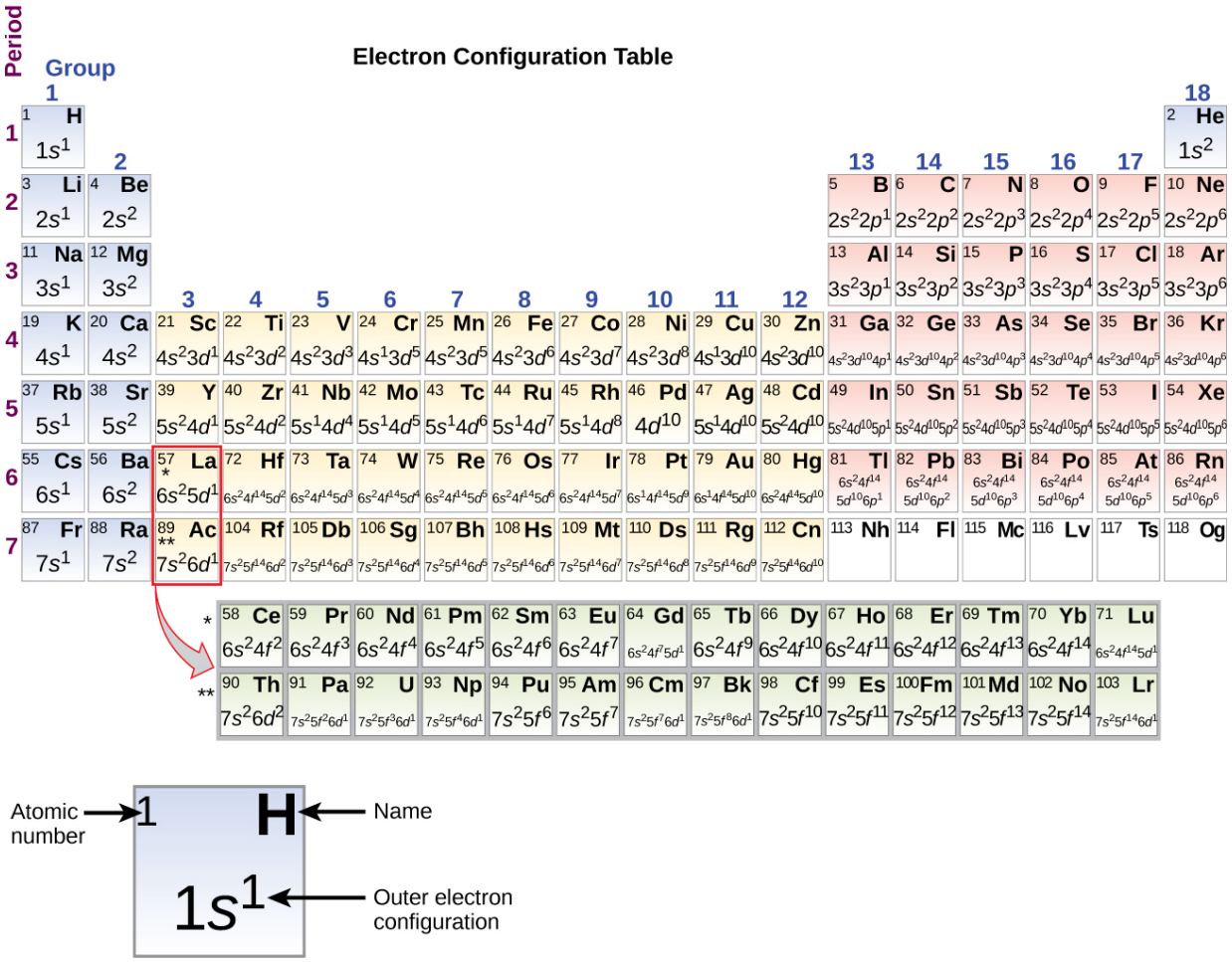


Figure **3.3.6**: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure **3.3.6**). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of [Ar]$4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of [Ar]$4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

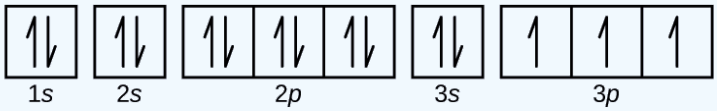
Example 3.3.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$

Exercise 3.3.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer

a. Mn
b. Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure **3.3.3**: or Figure **3.3.4**. For instance, the electron configurations (shown in Figure **3.3.6**) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

3.3.3: Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure **3.3.6**), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure **3.3.6**: , which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure **3.3.6**: show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure **3.3.6**. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure **3.3.6**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure **3.3.6**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure **3.3.6**. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    a. The lanthanide series: lanthanum (La) through lutetium (Lu)
    b. The actinide series: actinium (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

3.3.4: Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example **3.3.2**: Predicting Electron Configurations of Ions

What is the electron configuration of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

? Exercise 3.3.21

Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$? Which ion with a +3 charge has this configuration?

Answer

Tc^{2+}, Ru^{3+}

This page titled 3.3: Electronic Structure of Atoms (Electron Configurations) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **6.4: Electronic Structure of Atoms (Electron Configurations)** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.3.1: Extra-Orbital Origin and Shape

Learning Objectives

By the end of this section, you will be able to:

- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

3.3.1.1: Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns similar to those shown on Figure **3.3.1.1**. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

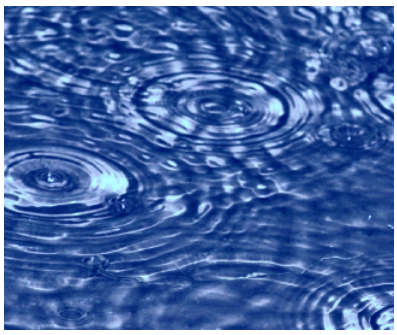


Figure **3.3.1.1**: An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the **de Broglie wavelength**. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure **3.3.1.2**).

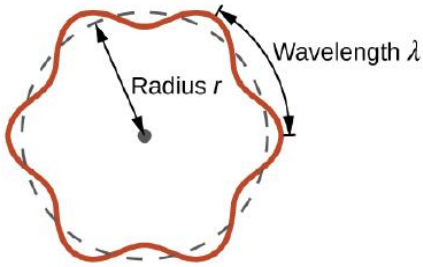


Figure **3.3.1.2**: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

For a circular orbit of radius r, the circumference is $2\pi r$, and so de Broglie's condition is:

$$2\pi r = n\lambda, \qquad n = 1, 2, 3, \ldots$$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure **3.3.1.3** shows an interference pattern. It is strikingly similar to the interference patterns for light shown in Electromagnetic Energy for light passing through two closely spaced, narrow slits. The wave–particle duality of matter can be seen in Figure **3.3.1.3** by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

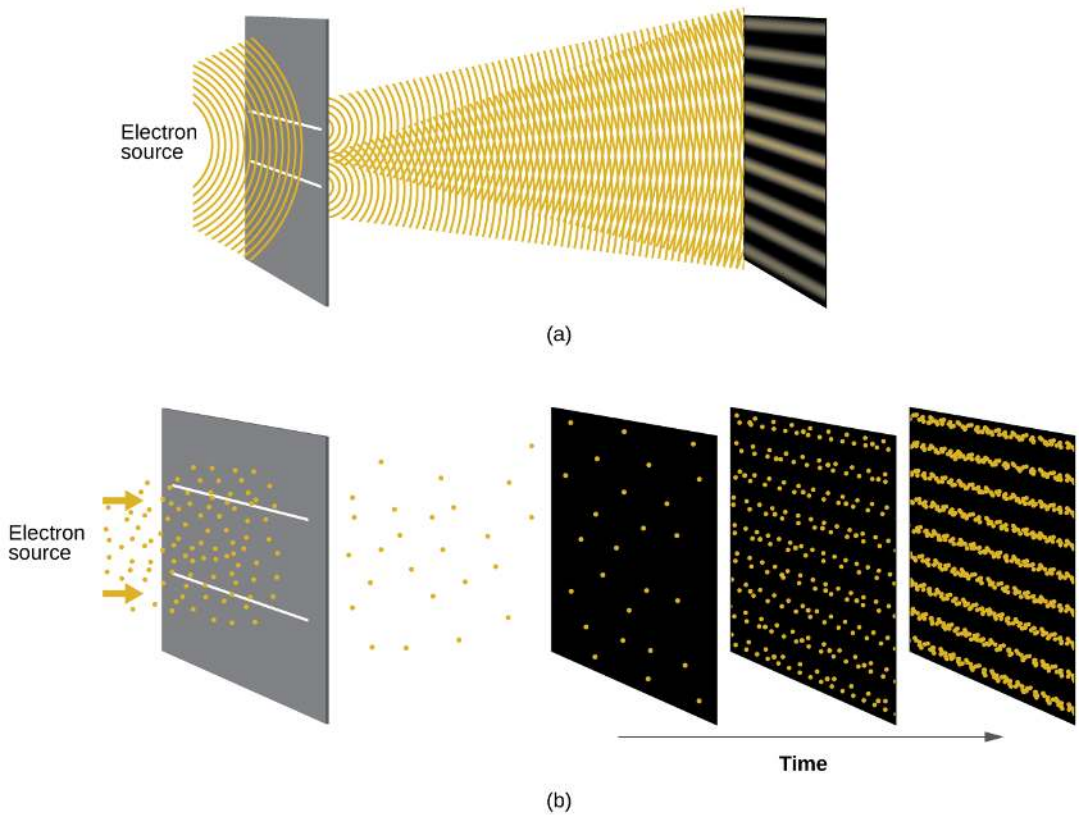


Figure **3.3.1.3**: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons.

Link to Learning

View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.

Example 3.3.1.1: Calculating the Wavelength of a Particle

If an electron travels at a velocity of $1.000 \times 10^7\ \text{m s}^{-1}$ and has a mass of $9.109 \times 10^{-28}\ \text{g}$, what is its wavelength?

Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that $1\ \text{J} = 1\text{kg m}^2/\text{s}^2$. Thus, we can write $h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$ as $6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}$.

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}}{(9.109 \times 10^{-31}\ \text{kg})\,(1.000 \times 10^7\ \text{m/s})} \\ &= 7.274 \times 10^{-11} m\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

Exercise 3.3.1.1

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer

1.9 10^{-34} m.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass \(m\) moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x, must be greater than or equal to $\hbar/2$ (where $\hbar = h/2$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position (Δx) has a value of, say, 1 pm (10^{-12} m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$\left[\Delta p = m\Delta v = \frac{\hbar}{(2\Delta x)}\right] = \frac{(1.055 \times 10^{-34}\,\mathrm{kg\,m^2/s})}{(2 \times 1 \times 10^{-12}\,\mathrm{m})} = 5 \times 10^{-23}\,\mathrm{kg\,m/s}$$

The value of $\hbar$ is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics.

Link to Learning

Read this article that describes a recent macroscopic demonstration of the uncertainty principle applied to microscopic objects.

3.3.1.2: The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, Erwin Schrödinger extended de Broglie's work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to

reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

$\hat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

Link to Learning

You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison.

3.3.1.3: Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure **3.3.1.4**). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

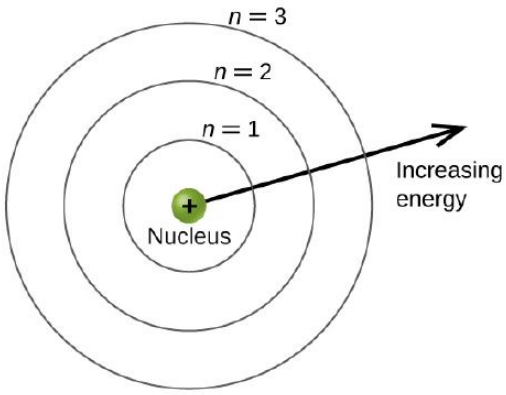


Figure **3.3.1.4**: Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= -2.18 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) J\end{aligned}$$

The values n_f and n_i are the final and initial energy states of the electron.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is l, the **secondary (angular momentum) quantum number**. It is an integer that may take the values, $l = 0, 1, 2, \ldots, n–1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n, defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital. Orbitals with the same value of l define a **subshell**.

Orbitals with $l = 0$ are called s orbitals and they make up the s subshells. The value $l = 1$ corresponds to the p orbitals. For a given n, p orbitals constitute a p subshell (e.g., 3p if n = 3). The orbitals with $l = 2$ are called the **d orbitals**, followed by the *f-*, *g-*, *and h-*orbitals for l = 3, 4, and 5.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a **radial node**. The number of radial nodes in an orbital is $n–l–1$.

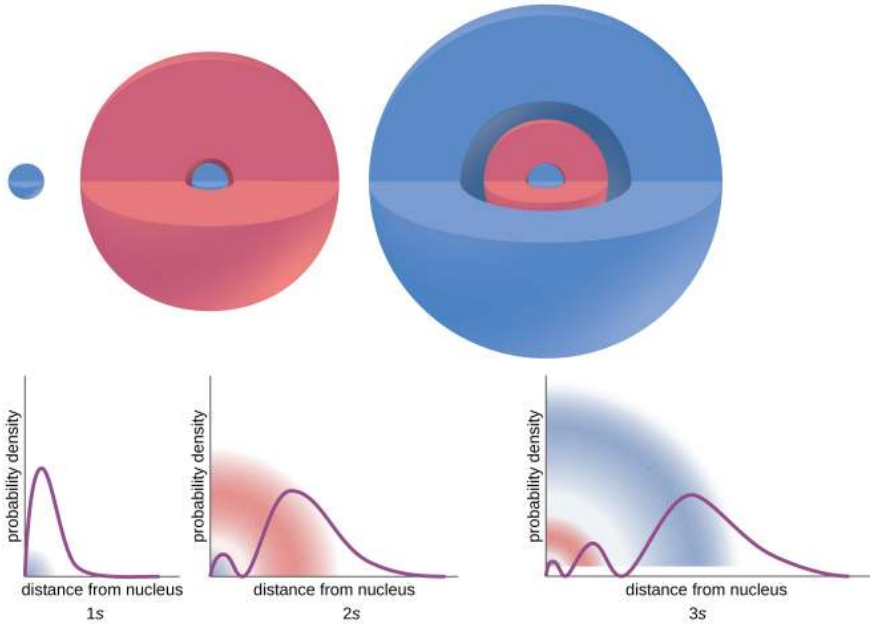


Figure **3.3.1.5**: The graphs show the probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus.

Consider the examples in Figure **3.3.1.5**. The orbitals depicted are of the *s* type, thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that there are 1 – 0 – 1 = 0 places where the density is zero (nodes) for 1*s* (*n* = 1), 2 – 0 – 1 = 1 node for 2*s*, and 3 – 0 – 1 = 2 nodes for the 3*s* orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

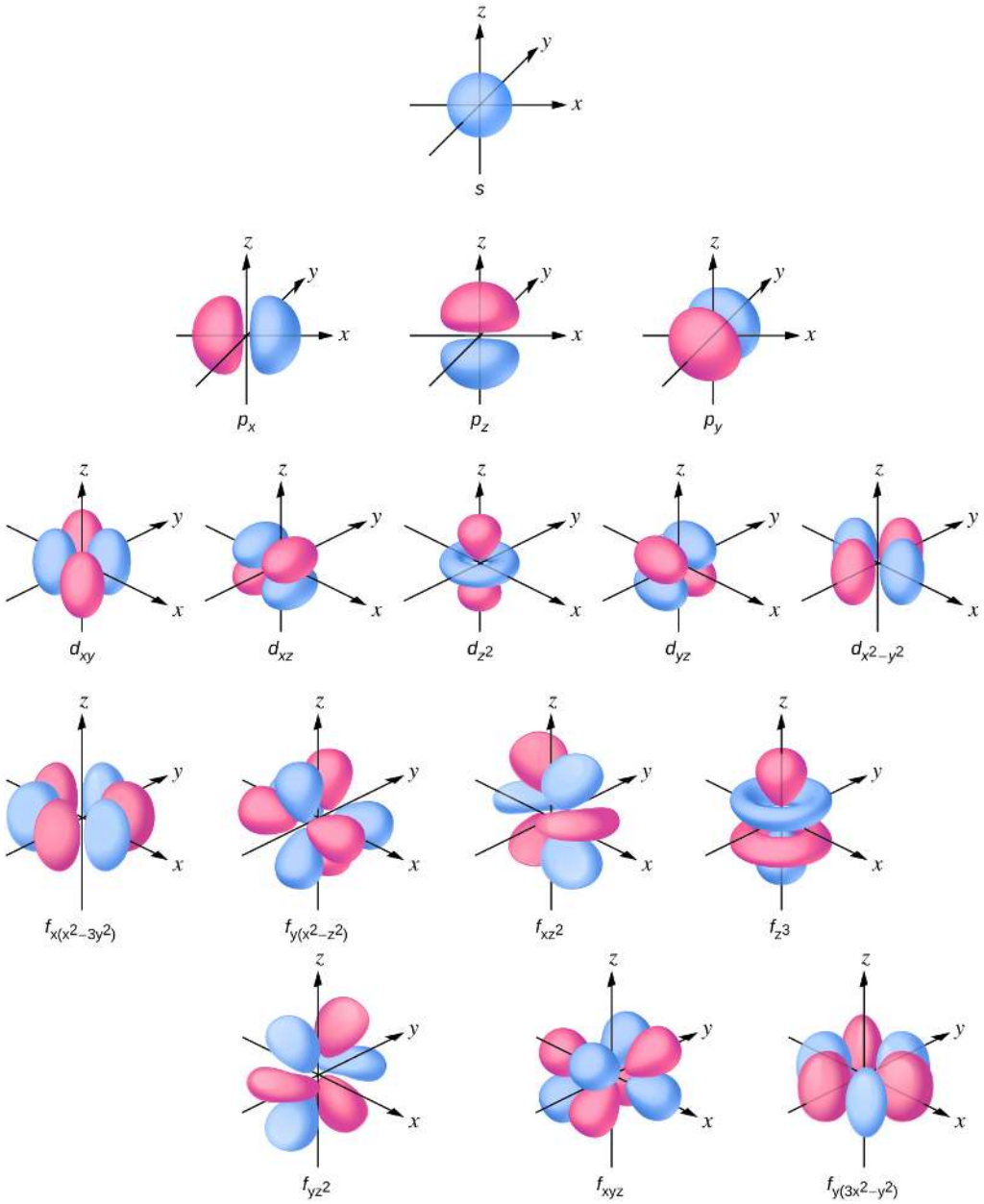


Figure **3.3.1.6**: Shapes of *s*, *p*, *d*, and *f* orbitals.

The **magnetic quantum number**, m_l, specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l are rangeed from $-l$ to $+l$, i.e.

$$-l, -(l-1), \ldots, 0, \ldots, (l-1), l\backslash).$$

The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l + 1$. Thus, there is one s-orbital in an s subshell ($l = 0$), there are three p-orbitals in a p subshell ($l = 1$), five d-orbitals in a d subshell (l = 2), seven f-orbitals in an f subshell ($l = 3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular

momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure **3.3.1.6**.

Figure **3.3.1.7** illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, n. The letter in the orbital name defines the subshell with a specific angular momentum quantum number l = 0 for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same n are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, n, are called degenerate orbitals. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure **3.3.1.7**. Orbitals within the same subshell are still degenerate and have the same energy.

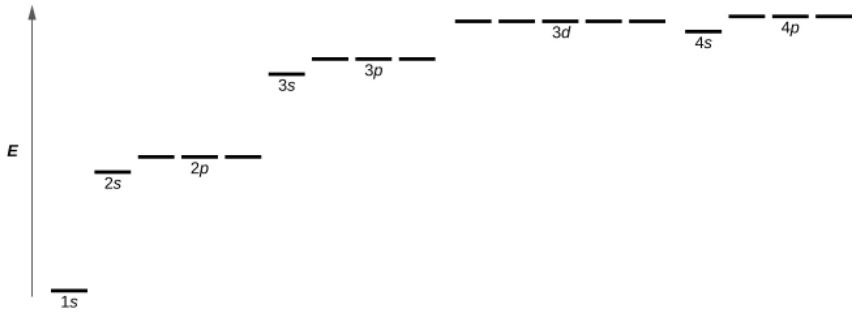


Figure **3.3.1.7**: The chart shows the energies of electron orbitals in a multi-electron atom.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or m_s.

The other three quantum numbers, n, l, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only “spin” in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = +1/2$. The other is called the $\beta state$, with the z component of the spin being negative and $m_s = -1/2$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = +1/2$ and $m_s = -1/2$ are different if an external magnetic field is applied.

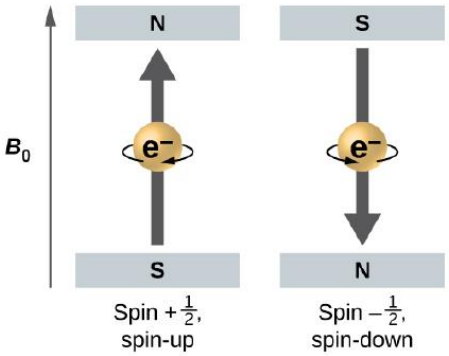


Figure **3.3.1.8**: Electrons with spin values in an external magnetic field.

Figure **3.3.1.8** illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $m_s = +1/2$ spin quantum number and down (in the negative z direction) for the spin quantum number of $m_s = -1/2$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure **3.3.1.8**) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = +1/2$ has a slightly lower energy in an external field in the positive z direction, and an electron with $m_s = -1/2$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

3.3.1.4: The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers *n*, *l*, and m_l) only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table **3.3.1.1**.

Table **3.3.1.1**: Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \le l \le n–1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \le m_l \le l$	orientation of the orbital
spin quantum number	m_s	$+\frac{1}{2}$ and $-\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

✔ Example **3.3.1.2**: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, s, p, d, and f subshells are found in the n = 4 shell of an atom. For $l = 0$ (the s subshell), m_l can only be 0. Thus, there is only one 4s orbital. For $l = 1$ (p-type orbitals), m can have values of –1, 0, +1, so we find three 4p orbitals. For l = 2 (d-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4d orbitals. When $l = 3$ (f-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

? Exercise 3.3.1.2

Identify the subshell in which electrons with the following quantum numbers are found:

a. n = 3, l = 1
b. n = 5, l = 3
c. n = 2, l = 0

Answer

a. 3*p*
b. 5*f*
c. 2s

✓ Example 3.3.1.3: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) n = 2, (b) n = 5, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

a. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
b. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
When $n = 5$, there are five subshells of orbitals that we need to sum:

$$\begin{array}{r} \text{1 orbital labeled 5s} \\ \text{3 orbitals labeled 5p} \\ \text{5 orbitals labeled 5d} \\ \text{7 orbitals labeled 5f} \\ +\ \text{9 orbitals labeled 5g} \\ \hline \text{25 orbitals total} \end{array}$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.
c. The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$.

? Exercise 3.3.1.3

If a shell contains a maximum of 32 electrons, what is the principal quantum number, n?

Answer

$n = 4$

Example 3.3.1.4: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is nl, where $l = 0, 1, 2, 3, 4, 5, ...$ is mapped to the letter sequence s, p, d, f, g, h, …,
- The m_l degeneracy is the number of orbitals within an l subshell, and so is $2l + 1$ (there is one s orbital, three p orbitals, five d orbitals, seven f orbitals, and so forth).
- The number of radial nodes is equal to $n–l–1$.

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 3.3.1.1

How many orbitals have $l = 2$ and $n = 3$?

Answer

The five degenerate 3*d* orbitals

This page titled 3.3.1: Extra-Orbital Origin and Shape is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **6.3: Development of Quantum Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.4: Ionic Bonding

Learning Objectives

By the end of this section, you will be able to:

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure **3.4.1**). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure **3.4.1**: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

3.4.1: The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3,

indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, (2 +3) + (3 –2) = 0].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure **3.4.2**).

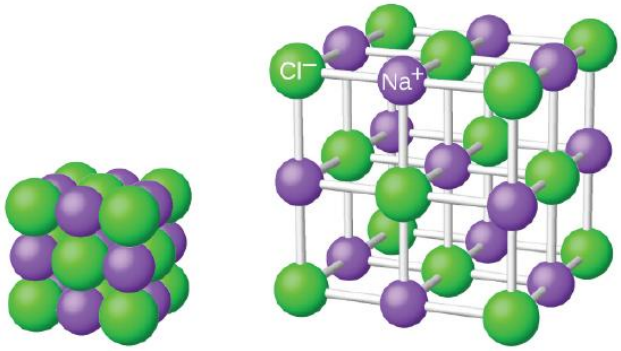


Figure **3.4.2**: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl\,(s) \longrightarrow Na^+\,(g) + Cl^-\,(g)} \qquad \Delta H = 769\,\mathrm{kJ}$$

3.4.2: Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons.

Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 3.4.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[Ar]3d^{10}4s^2$

Cr: $[Ar]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

Zn^{2+}: $[Ar]3d^{10}$

Cr^{3+}: $[Ar]3d^3$

Exercise 3.4.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

3.4.3: Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 3.4.1: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^2 4p^6$

I^-: $[Kr]4d^{10}5s^2 5p^6$

Exercise 3.4.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: [Ne]$3s^2 3p^3$; P^{3-}: [Ne]$3s^2 3p^6$

This page titled 3.4: Ionic Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **7.1: Ionic Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.5: Covalent Bonding

Learning Objectives

By the end of this section, you will be able to:

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

3.5.1: Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure **3.5.1** illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

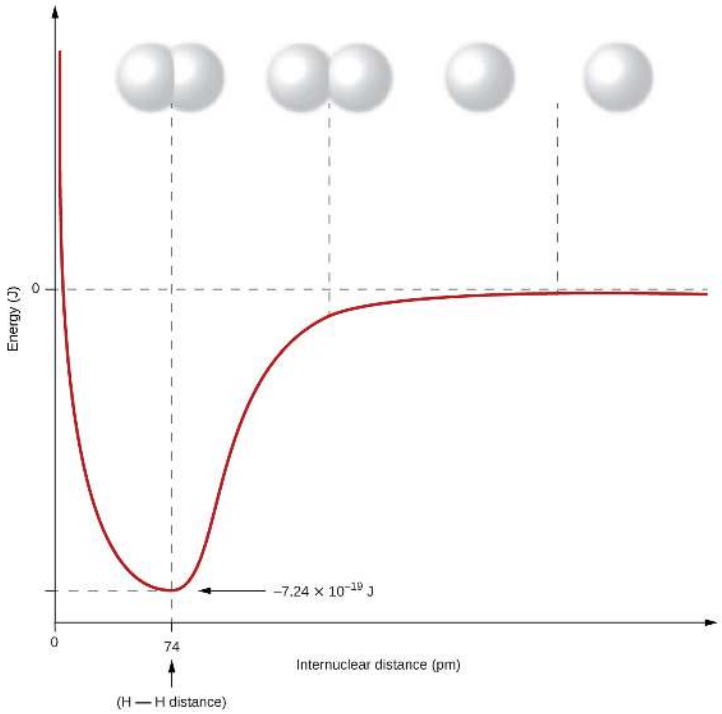


Figure **3.5.1**: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2\,(g) \longrightarrow 2\,H\,(g)} \quad \Delta H = 436\,\mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$\mathrm{2\,H\,(g) \longrightarrow H_2\,(g)} \quad \Delta H = -436\,\mathrm{kJ}$$

3.5.2: Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl + Cl \longrightarrow Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure **3.5.2** shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is

much larger than it is around H. Compare this to Figure **3.5.1**, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure **3.5.2**.

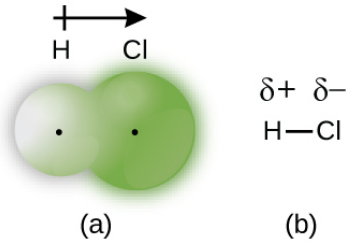


Figure **3.5.2**: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

3.5.3: Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure **3.5.3** shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure **3.5.4**). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

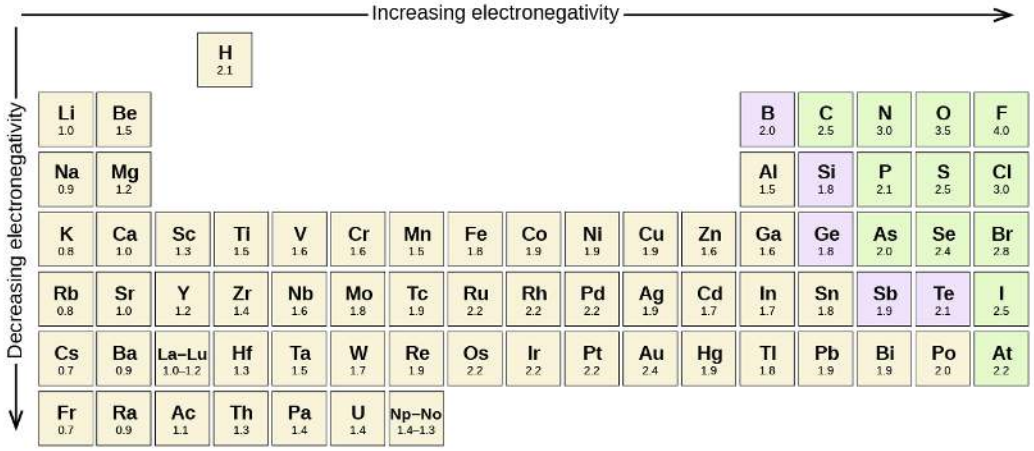


Figure **3.5.3**: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

3.5.3.1: Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless

quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure **3.5.4**, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

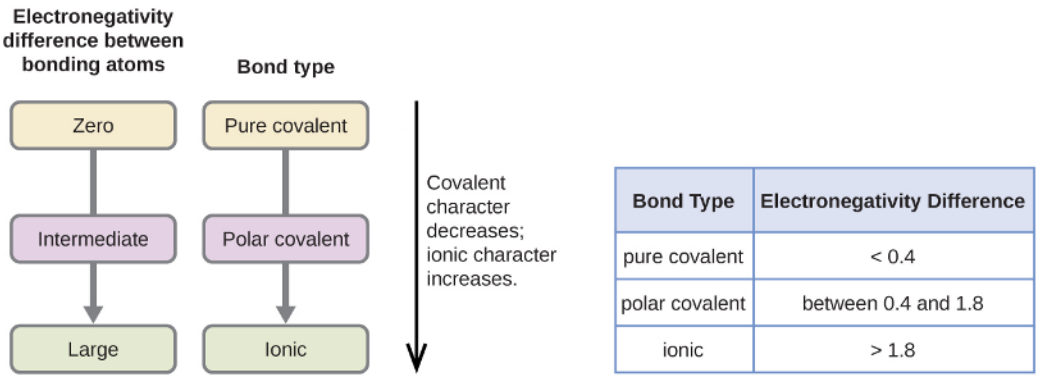


Figure **3.5.4**: Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

3.5.3.2: Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure **3.5.5** shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure **3.5.5**: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure **3.5.5**. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that

are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, and are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and as well as covalent between the nitrogen and oxygen atoms in

Example 3.5.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure **3.5.3**, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table **3.5.1** shows these bonds in order of increasing polarity.

Table **3.5.1**: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	
S–H	0.4	
C–N	0.5	
N–H	0.9	
C–O	1.0	
O–H	1.4	

Exercise 3.5.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure **3.5.3**, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	
Si–C	0.7	
Si–O	1.7	

This page titled 3.5: Covalent Bonding is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **7.2: Covalent Bonding** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

3.6: Exercises

1.

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

2.

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^{8}\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

3.

FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^{7}\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

4.

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

5.

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV ($1\ eV = 1.602 \times 10^{-19}$ J)?

6.

Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

7.

A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

8.

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

9.

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

10.

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

11.

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

12.

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

13.

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

14.

Answer the following questions about a Blu-ray laser:

(a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?

(b) A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?

(c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = $0.60(\lambda/\text{NA})$, where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?

(d) The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^{7} bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

15.

What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects an electron with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

16.

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

17.

What does it mean to say that the energy of the electrons in an atom is quantized?

18.

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

19.

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602×10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

20.

Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

21.

Using the Bohr model, determine the lowest possible energy for the electron in the He^{+} ion.

22.

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

23.

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

24.

How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

25.

What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

26.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^{+} ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.

27.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

28.

Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1$, 2, 3, and 4 orbits.

(a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbits?

(b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).

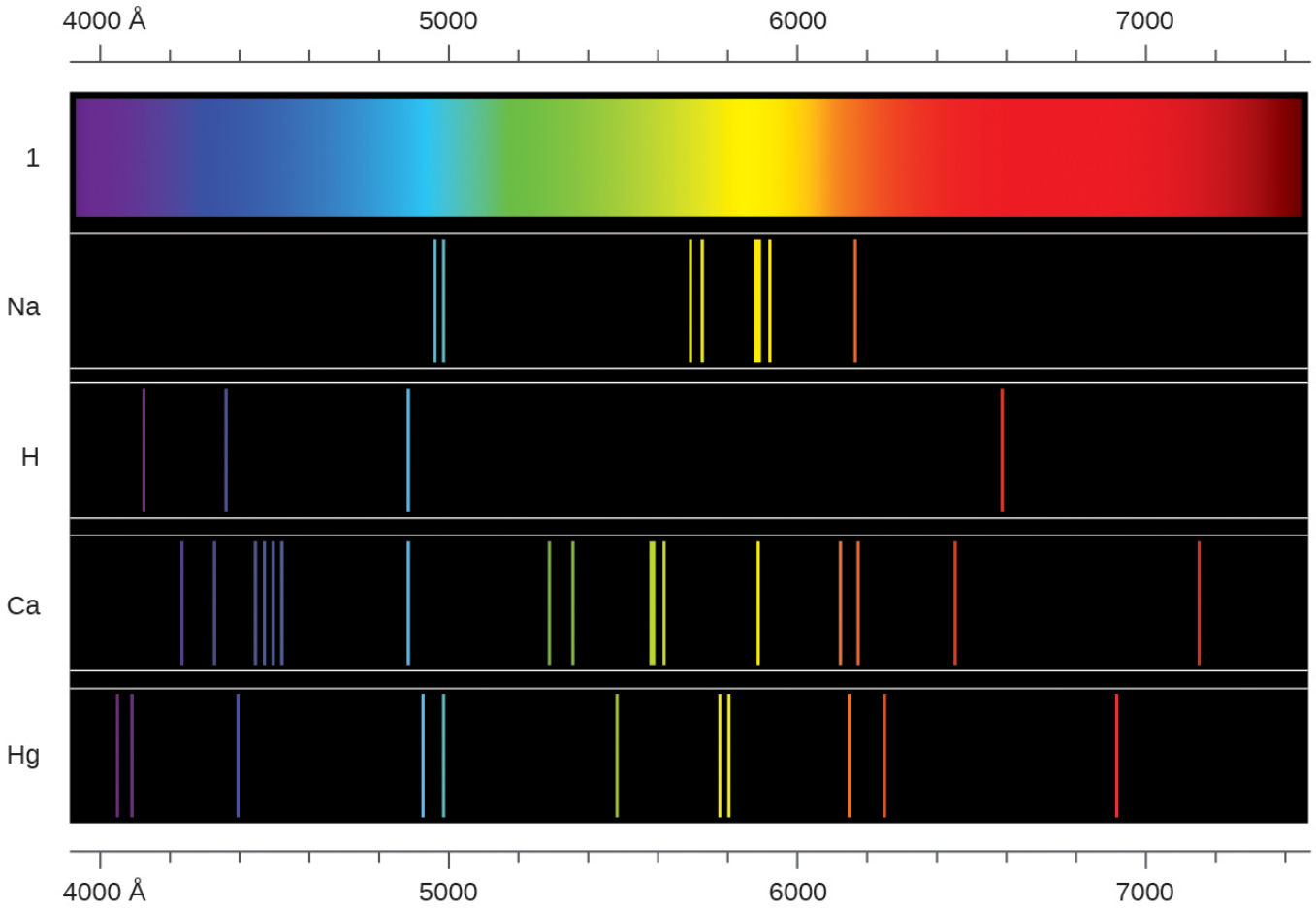
(c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

29.

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

30.

The spectra of hydrogen and of calcium are shown here.



What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

31.

How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

32.

What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

33.

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

34.

Answer the following questions:

(a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.

(b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

35.

Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 2$, $l = 1$

(b) $n = 4$, $l = 2$

(c) $n = 6$, $l = 0$

36.

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

37.

Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 3$, $l = 2$

(b) $n = 1$, $l = 0$

(c) $n = 4$, $l = 3$

38.

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

39.

Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

40.

Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

41.

Consider the orbitals shown here in outline.



(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?

(b) How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?

(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.

(d) What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?

(e) What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

42.

State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

43.

How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

44.

Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

(a) $c = \lambda\nu$

(b) $E = \frac{mv^2}{2}$

(c) $r = \frac{n^2 a_0}{Z}$

(d) $E = h\nu$

(e) $\lambda = \frac{h}{mv}$

45.

Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

46.

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

47.

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

48.

Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Sm

49.

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) N

(b) Si

(c) Fe

(d) Te

(e) Tb

50.

Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

51.

What additional information do we need to answer the question "Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$"?

52.

Draw the orbital diagram for the valence shell of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Ru

53.

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

(a) N

(b) Si

(c) Fe

(d) Te

(e) Mo

54.

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

(a) N^{3-}

(b) Ca^{2+}

(c) S^{-}

(d) Cs^{2+}

(e) Cr^{2+}

(f) Gd^{3+}

55.

Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

56.

Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?

57.

Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a –2 charge has this configuration?

58.

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

59.

Which of the following has two unpaired electrons?

(a) Mg

(b) Si

(c) S

(d) Both Mg and S

(e) Both Si and S.

60.

Which atom would be expected to have a half-filled 6*p* subshell?

61.

Which atom would be expected to have a half-filled 4*s* subshell?

62.

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

63.

Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

64.

Write the electron configurations for the following atoms or ions:

(a) B^{3+}

(b) O^{-}

(c) Cl^{3+}

(d) Ca^{2+}

(e) Ti

65.

Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

66.

Write a set of quantum numbers for each of the electrons with an *n* of 3 in a Sc atom.

67.

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

68.

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

69.

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

70.

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

71.

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

72.

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: Mg, O, S, Si

73.

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

74.

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

75.

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

76.

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

77.

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

78.

List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.

79.

Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

80.

Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

81.

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Mg^{2+}.

82.

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: Note the process depicted does *not* correspond to electron affinity.)

$$\mathrm{E^+}(g) + \mathrm{e^-} \longrightarrow \mathrm{E}(g)$$

83.

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$\mathrm{E}(g) \longrightarrow \mathrm{E^+}(g) + \mathrm{e^-}$$

84.

The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

85.

Which main group atom would be expected to have the lowest second ionization energy?

86.

Explain why Al is a member of group 13 rather than group 3?

87.

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) uranium

(b) bromine

(c) strontium

(d) neon

(e) gold

(f) americium

(g) rhodium

(h) sulfur

(i) carbon

(j) potassium

88.

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) cobalt

(b) europium

(c) iodine

(d) indium

(e) lithium

(f) oxygen

(g) cadmium

(h) terbium

(i) rhenium

89.

Using the periodic table, identify the lightest member of each of the following groups:

(a) noble gases

(b) alkaline earth metals

(c) alkali metals

(d) chalcogens

90.

Using the periodic table, identify the heaviest member of each of the following groups:

(a) alkali metals

(b) chalcogens

(c) noble gases

(d) alkaline earth metals

91.

Use the periodic table to give the name and symbol for each of the following elements:

(a) the noble gas in the same period as germanium

(b) the alkaline earth metal in the same period as selenium

(c) the halogen in the same period as lithium

(d) the chalcogen in the same period as cadmium

92.

Use the periodic table to give the name and symbol for each of the following elements:

(a) the halogen in the same period as the alkali metal with 11 protons

(b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons

(c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons

(d) the noble gas in the same period as gold

93.

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the alkali metal with 11 protons and a mass number of 23

(b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom

(c) the isotope with 33 protons and 40 neutrons in its nucleus

(d) the alkaline earth metal with 88 electrons and 138 neutrons

94.

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the chalcogen with a mass number of 125

(b) the halogen whose longest-lived isotope is radioactive

(c) the noble gas, used in lighting, with 10 electrons and 10 neutrons

(d) the lightest alkali metal with three neutrons

95.

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

96.

Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

97.

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

(a) NF_3

(b) BaO,

(c) $(NH_4)_2CO_3$

(d) $Sr(H_2PO_4)_2$

(e) IBr

(f) Na_2O

98.

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

(a) $KClO_4$

(b) $Mg(C_2H_3O_2)_2$

(c) H_2S

(d) Ag_2S

(e) N_2Cl_4

(f) $Co(NO_3)_2$

99.

For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

(a) Ca^{2+}, S^{2-}

(b) $\mathbf{NH_4^+}$, $\mathbf{SO_4^{2-}}$

(c) Al^{3+}, Br^-

(d) Na^+, $\mathbf{HPO_4^{2-}}$

(e) Mg^{2+}, $\mathbf{PO_4^{3-}}$

100.

For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

(a) K^+, O^{2-}

(b) $\mathbf{NH_4^+}$, $\mathbf{PO_4^{3-}}$

(c) Al^{3+}, O^{2-}

(d) Na^+, $\mathbf{CO_3^{2-}}$

(e) Ba^{2+}, $\mathbf{PO_4^{3-}}$

This page titled 3.6: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

3.6.1: Answers to Selected Exercises

1.

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

3.

3.15 m

5.

3.233×10^{-19} J; 2.018 eV

7.

$\nu = 4.568 \times 10^{14}$ s^{-1}; $\lambda = 656.3$ nm; Energy $mol^{-1} = 1.823 \times 10^{5}$ J mol^{-1}; red

9.

(a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The color of (a) is red; (b) is blue.

11.

$E = 9.502 \times 10^{-15}$ J; $\nu = 1.434 \times 10^{19}$ s^{-1}

13.

Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

15.

5.49×10^{14} s^{-1}; no

17.

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

19.

2.856 eV

21.

-8.716×10^{-18} J

23.

-3.405×10^{-20} J

25.

33.9 Å

27.

1.471×10^{-17} J

29.

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single

quantum number, n. The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

31.

Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, n = 1, 2, 3, …, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [s orbitals] can have zero angular momentum).

33.

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_1 determines the orientation of the orbitals of the same l value with respect to one another. m_s determines the spin of an electron.

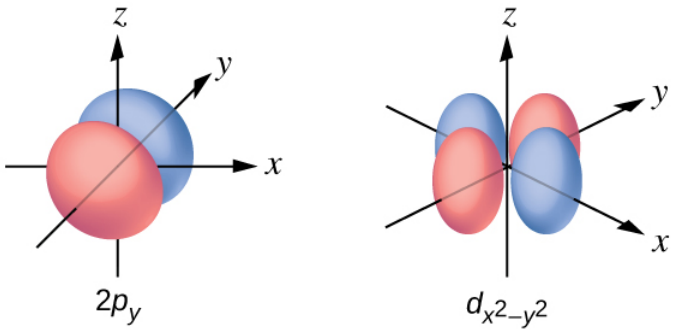
35.

(a) 2*p*; (b) 4*d*; (c) 6*s*

37.

(a) 3*d;* (b) 1*s;* (c) 4*f*

39.



41.

(a) x. 2, y. 2, z. 2; (b) x. 1, y. 3, z. 0; (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$; (d) x. 1, y. 2, z. 3; (e) x. l = 0, m_l = 0, y. l = 1, m_l = –1, 0, or +1, z. l = 2, m_l = –2, –1, 0, +1, +2

43.

12

45.

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

47.

For example, Na^+: $1s^22s^22p^6$; Ca^{2+}: $1s^22s^22p^63s^23p^6$; Sn^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$; F^-: $1s^22s^22p^6$; O^{2-}: $1s^22s^22p^6$; Cl^-: $1s^22s^22p^63s^23p^6$.

49.

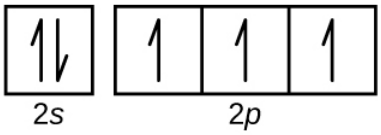
(a) $1s^22s^22p^3$; (b) $1s^22s^22p^63s^23p^2$; (c) $1s^22s^22p^63s^23p^64s^23d^6$; (d) $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$; (e) $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^9$

51.

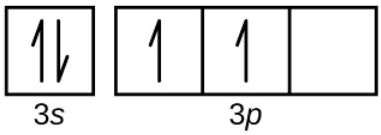
The charge on the ion.

53.

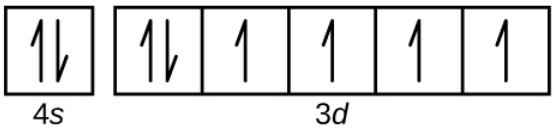
(a)



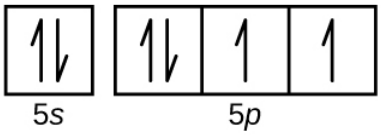
(b)



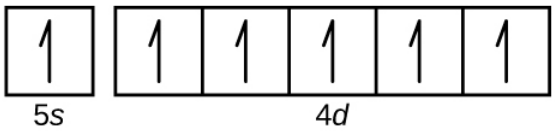
(c)



(d)



(e)



55.

Zr

57.

Rb^{+}, Se^{2-}

59.

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

61.

K

63.

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10}$

65.

Co has 27 protons, 27 electrons, and 33 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$. I has 53 protons, 53 electrons, and 78 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$.

67.

Cl

69.

O

71.

Rb < Li < N < F

73.

15 (5A)

75.

Mg < Ca < Rb < Cs

77.

$Si^{4+} < Al^{3+} < Ca^{2+} < K^{+}$

79.

Se, As^{-}

81.

$Mg^{2+} < K^{+} < Br^{-} < As^{3-}$

83.

O, IE_1

85.

Ra

87.

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal,

representative element; (i) nonmetal, representative element; (j) metal, representative element

89.

(a) He; (b) Be; (c) Li; (d) O

91.

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

93.

(a) $^{23}_{11}\mathrm{Na}$; (b) $^{129}_{54}\mathrm{Xe}$; (c) $^{73}_{33}\mathrm{As}$; (d) $^{226}_{88}\mathrm{Ra}$

95.

Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

97.

(a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, $\mathrm{NH_4^+}$, $\mathrm{CO_3^{2-}}$; (d) ionic, Sr^{2+}, $\mathrm{H_2PO_4^-}$; (e) covalent; (f) ionic, Na^+, O^{2-}

99.

(a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3\,(PO_4)_2$

This page titled 3.6.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

4: Lewis Structures; Geometry and Polarity of Molecules

4.1: Lewis Symbols and Structures

4.1.1: Extra-Formal Charges and Resonance

4.2: Molecular Structure and Polarity

4.3: Hybrid Atomic Orbitals

4.3.1: Extra-Multiple Bonds

4.4: Intermolecular Forces

4.4.1: Extra-Properties of Liquids

4.5: Exercises (Lewis Structures)

4.5.1: Answers to Selected Exercises

4.6: Exercises (Intermolecular Forces)

4.6.1: Answers to Selected Exercises

This page titled 4: Lewis Structures; Geometry and Polarity of Molecules is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

4.1: Lewis Symbols and Structures

Learning Objectives

By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

4.1.1: Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 4.1.1: shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na•
magnesium	$[Ne]3s^2$	•Mg•
aluminum	$[Ne]3s^23p^1$	•Al•
silicon	$[Ne]3s^23p^2$	•Si•
phosphorus	$[Ne]3s^23p^3$	•P•
sulfur	$[Ne]3s^23p^4$	:S•
chlorine	$[Ne]3s^23p^5$	:Cl•
argon	$[Ne]3s^23p^6$	:Ar:

Figure 4.1.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



Figure 4.1.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

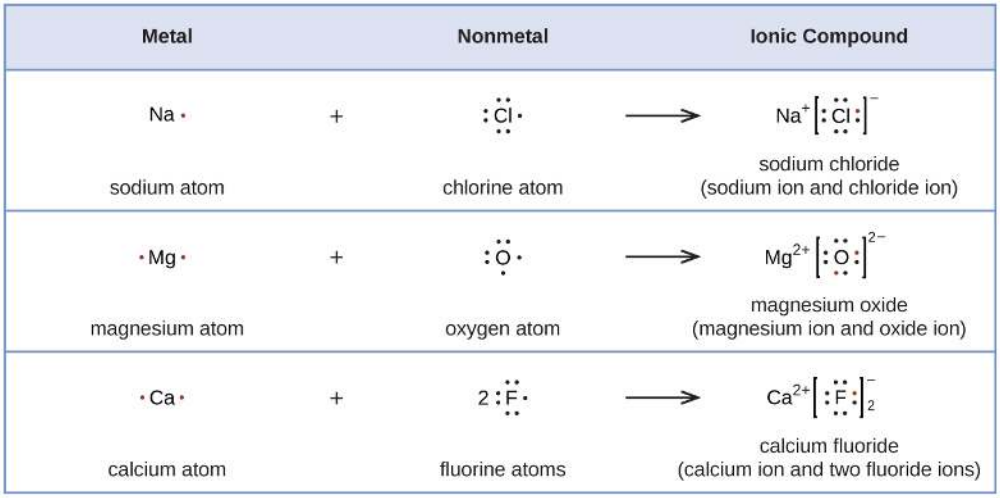
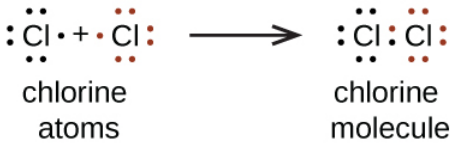


Figure **4.1.2**: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

4.1.2: Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

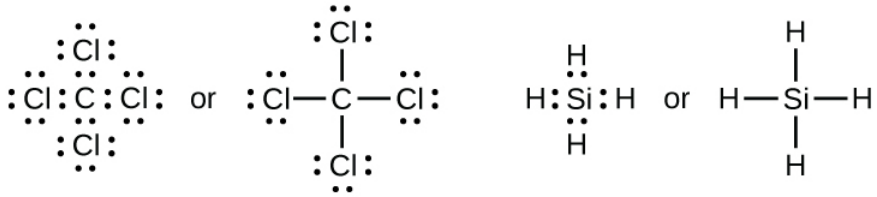


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

4.1.2.1: The Octet Rule

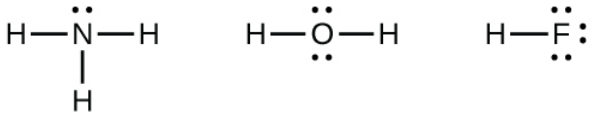
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



carbon tetrachloride silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

4.1.2.2: Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

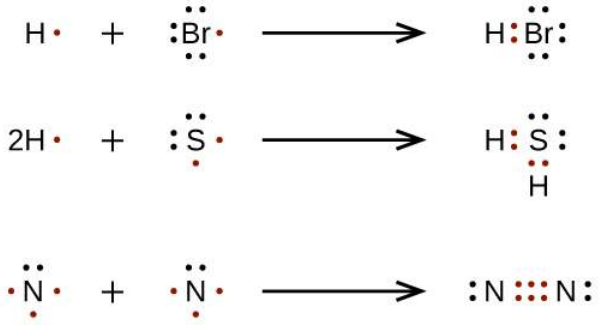
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

4.1.3: Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here.

Writing Lewis Structures

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of $\mathbf{SiH_4}$, $\mathbf{CHO_2^-}$, $\mathbf{NO^+}$, and $\mathbf{OF_2}$ as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{array}{r} \mathbf{SiH_4} \\ \mathbf{Si:\ 4\ valence\ electrons/atom \times\ 1\ atom\ = 4} \\ \mathbf{+\quad H:\ 1\ valence\ electron/atom \times\ 4\ atoms = 4} \\ \hline \mathbf{total\ valence\ electrons = 8} \end{array}$$

   - For a *negative ion*, such as $\mathbf{CHO_2^-}$, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{array}{r} \mathbf{CHO_2^-} \\ \mathbf{C:\ 4\ valence\ electrons/atom \times\ 1\ atom\ = 4} \\ \mathbf{H:\ 1\ valence\ electron/atom \times\ 1\ atoms = 1} \\ \mathbf{O:\ 6\ valence\ electron/atom \times\ 2\ atoms = 12} \\ \mathbf{+\quad 1\ electron = 1} \\ \hline \mathbf{total\ valence\ electrons = 18} \end{array}$$

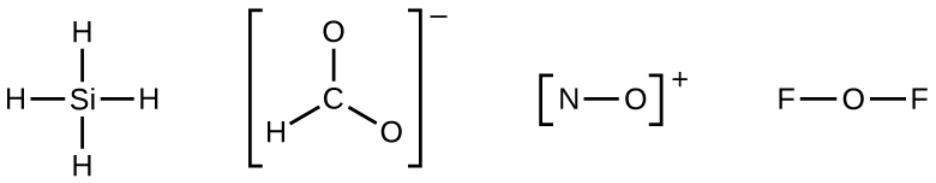
   - For a *positive ion*, such as $\mathbf{NO^+}$, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{array}{r} \mathrm{NO^+} \\ \text{N: 5 valence electrons/atom} \times \text{ 1 atom } = 5 \\ \text{O: 6 valence electron/atom} \times \text{ 1 atoms} = 6 \\ + \quad \text{e: -1 electron (positive charge)} \times \text{ 1 electron} = -1 \\ \hline \text{total valence electrons} = 10 \end{array}$$

- Since $\mathrm{OF_2}$ is a neutral molecule, we simply add the number of valence electrons:

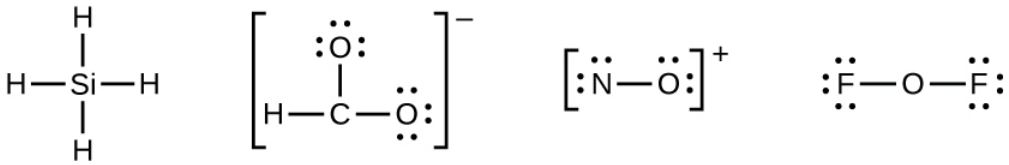
$$\begin{array}{r} \mathrm{OF_2} \\ \text{O: 6 valence electrons/atom} \times \text{ 1 atom } = 6 \\ + \quad \text{F: 7 valence electron/atom} \times \text{ 2 atoms} = 14 \\ \hline \text{total valence electrons} = 20 \end{array}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)

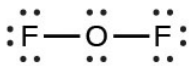


When several arrangements of atoms are possible, as for $\mathrm{CHO_2^-}$, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In $\mathrm{CHO_2^-}$, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $\mathrm{POCl_3}$, S in $\mathrm{SO_2}$, and Cl in $\mathrm{ClO_4^-}$. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

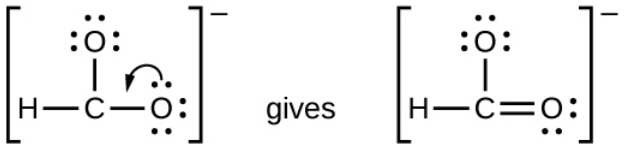
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on $\mathrm{SiH_4}$, so it is unchanged:



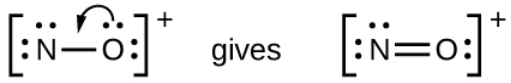
4. Place all remaining electrons on the central atom.
   - For $\mathrm{SiH_4}$, $\mathrm{CHO_2^-}$, and $\mathrm{NO^+}$, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For $\mathrm{OF_2}$, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



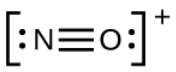
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - $\mathrm{SiH_4}$: Si already has an octet, so nothing needs to be done.
   - $\mathrm{CHO\ 2^-}$: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 4.1.1: Writing Lewis Structures

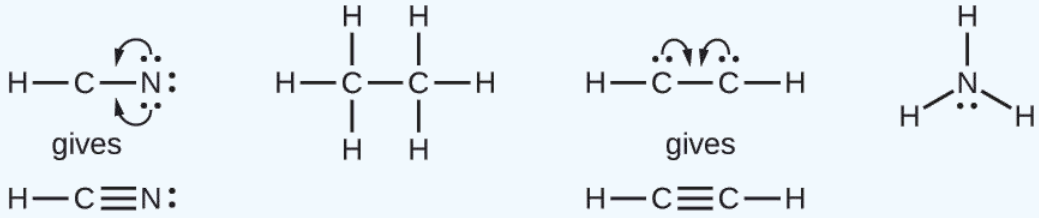
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

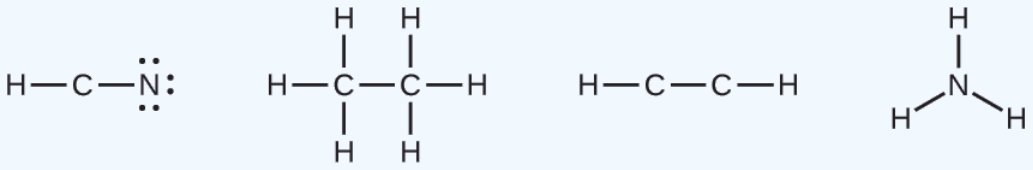
Step 1. *Calculate the number of valence electrons.*

HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
NH_3: (5 × 1) + (3 × 1) = 8

Step 2 *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom:

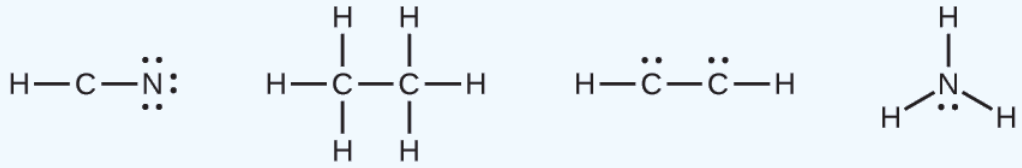


Step 3. *Where needed, distribute electrons to the terminal atoms:*



HCN: six electrons placed on N
H_3CCH_3: no electrons remain
HCCH: no terminal atoms capable of accepting electrons
NH_3: no terminal atoms capable of accepting electrons

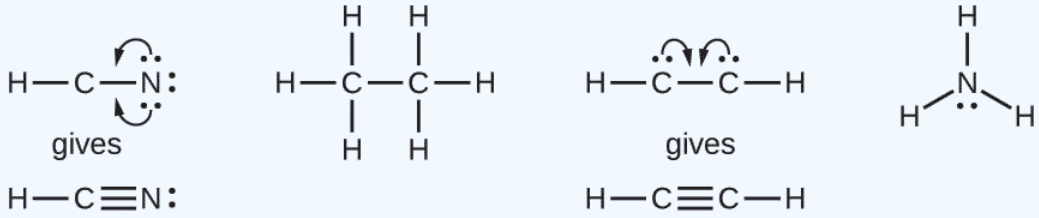
Step 4. *Where needed, place remaining electrons on the central atom:*



HCN: no electrons remain
H_3CCH_3: no electrons remain
HCCH: four electrons placed on carbon
NH_3: two electrons placed on nitrogen

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

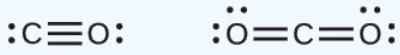
HCN: form two more C–N bonds
H_3CCH_3: all atoms have the correct number of electrons
HCCH: form a triple bond between the two carbon atoms
NH_3: all atoms have the correct number of electrons



? Exercise 4.1.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times, . Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steelmaking process, and diamonds have a unique place in both culture and industry. With all this usage came significant study, particularly with the emergence of organic chemistry. And even with all the known forms and functions of the element, scientists began to uncover the potential for even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu—they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure **4.1.3**), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

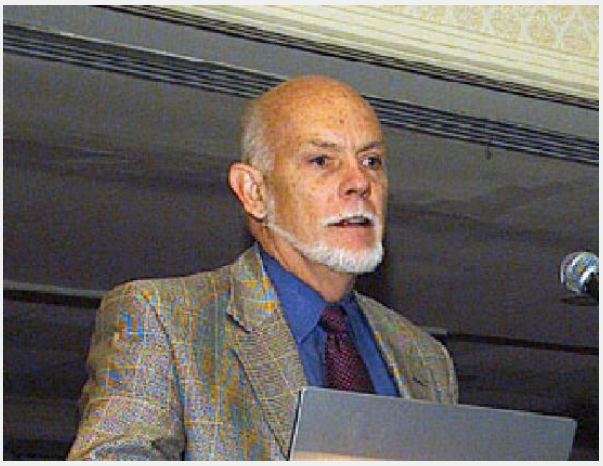


Figure **4.1.3**: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

4.1.4: Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

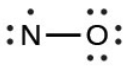
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

4.1.4.1: Odd-electron Molecules

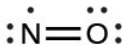
We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

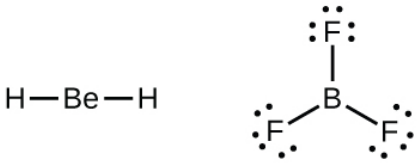


4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

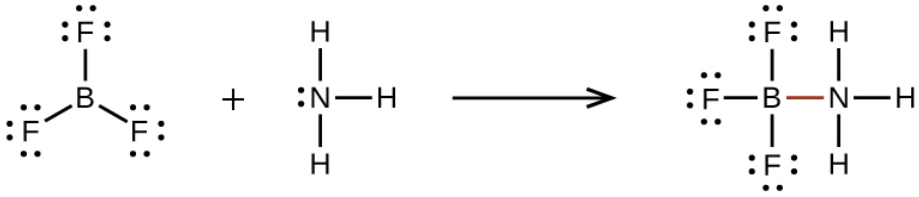


4.1.4.2: Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



4.1.4.3: Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure **4.1.4**: shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

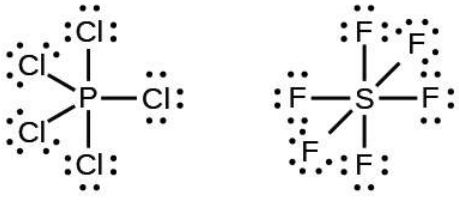
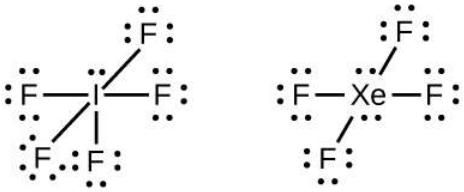


Figure **4.1.4**: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 4.1.2: Writing Lewis Structures - Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

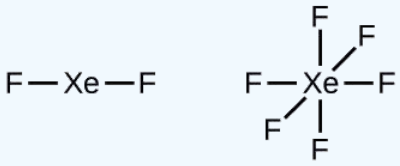
Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

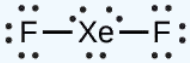
XeF_2: $8 + (2 \times 7) = 22$
XeF_6: $8 + (6 \times 7) = 50$

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

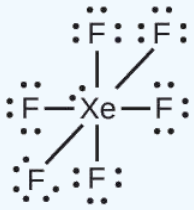


Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:

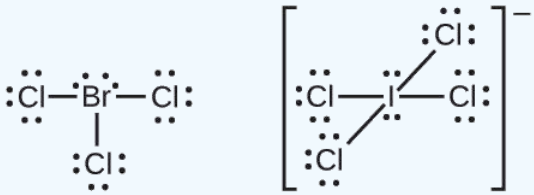


https://chem.libretexts.org/@go/page/432921

Exercise 4.1.2: Interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer



This page titled 4.1: Lewis Symbols and Structures is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **7.3: Lewis Symbols and Structures** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.1.1: Extra-Formal Charges and Resonance

Learning Objectives

By the end of this section, you will be able to:

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

4.1.1.1: Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge } = \#\text{ valence shell electrons (free atom) } - \#\text{ lone pair electrons } - \frac{1}{2}\#\text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

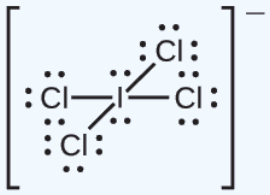
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 4.1.1.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion

Solution

Step 1. *We divide the bonding electron pairs equally for all I–Cl bonds:*



Step 2. *We assign lone pairs of electrons to their atoms*. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom:*

I: 7 – 8 = –1
Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 4.1.1.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

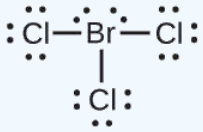
C −1, O +1

Example 4.1.1.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Step 1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



Step 2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge:

Br: 7 – 7 = 0
Cl: 7 – 7 = 0

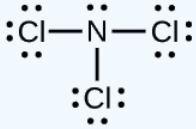
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 4.1.1.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0

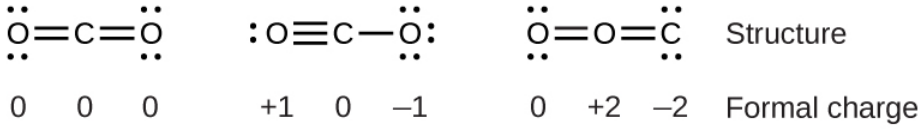


4.1.1.2: Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

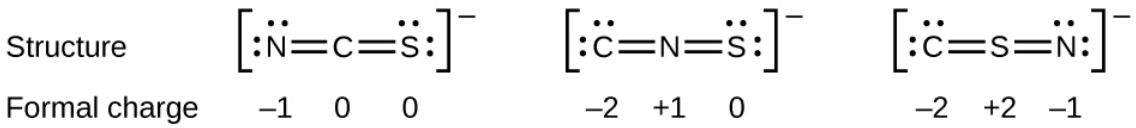
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

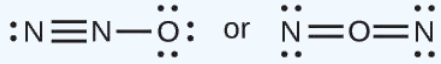
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: NCS^-, CNS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

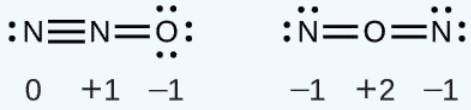
Example 4.1.1.3: Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the more likely structure for nitrous oxide?

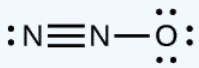


Solution

Determining formal charge yields the following:



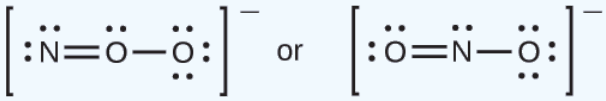
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), there is no formal charge with a magnitude greater than one (Guideline 2), the negative formal charge is on the more electronegative element (Guideline 4), and the less electronegative atom is in the center position.

Exercise 4.1.1.3

Which is the most likely molecular structure for the nitrite ion?



Answer

ONO^-

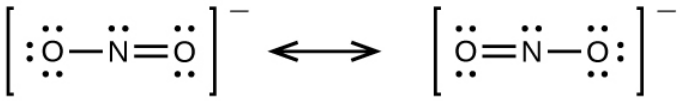
4.1.1.3: Resonance

Notice that the more likely structure for the nitrite anion in Example **4.1.1.3** may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:



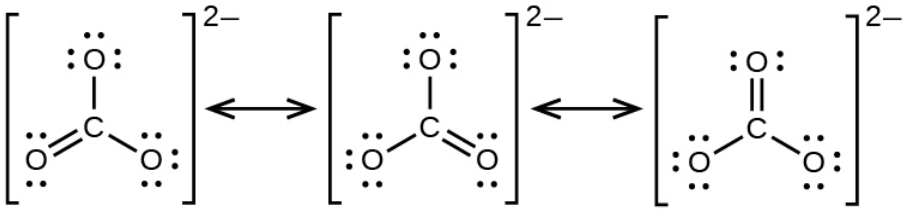
If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Link to Learning

Use this online quiz to practice your skills in drawing resonance structures and estimating formal charges.

This page titled 4.1.1: Extra-Formal Charges and Resonance is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **7.4: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.2: Molecular Structure and Polarity

Learning Objectives

By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure **4.2.1**). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

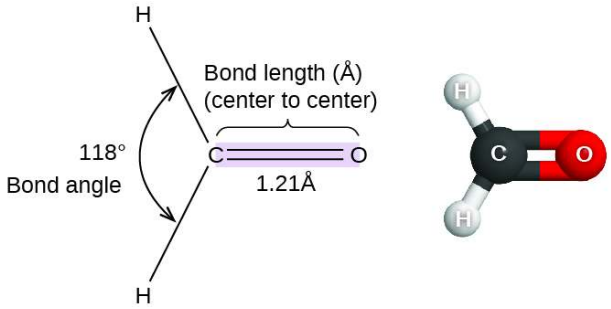


Figure **4.2.1**: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

4.2.1: VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure **4.2.2**) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure **4.2.2**).

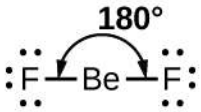


Figure **4.2.2**: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure **4.2.3** illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three

regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

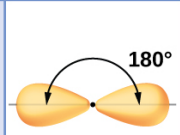
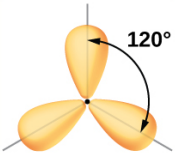
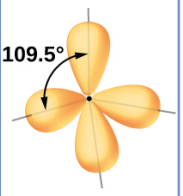
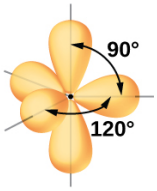
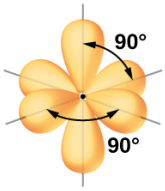
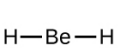
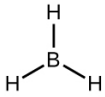
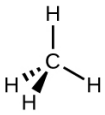
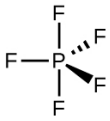
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure **4.2.3**: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

4.2.1.1: Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure **4.2.3** describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

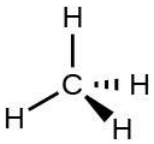


Figure **4.2.4**: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure **4.2.4**). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure **4.2.5**).

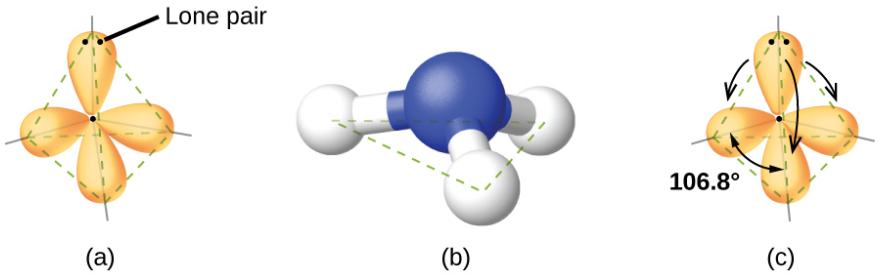


Figure **4.2.5**: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in Figure **4.2.5**, small distortions from the ideal angles in Figure **4.2.3** can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure **4.2.1**). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure **4.2.5**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure **4.2.3**) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure **4.2.5**). Figure **4.2.6** illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

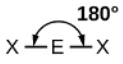
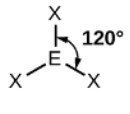
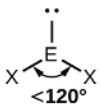
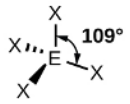
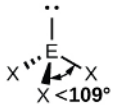
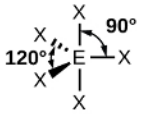
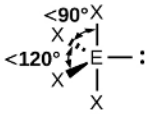
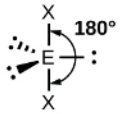
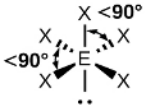
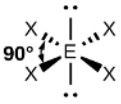
Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure **4.2.6**: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure **4.2.6**) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure **4.2.7** an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). As shown in Figure **4.2.6**, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure **4.2.7**). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

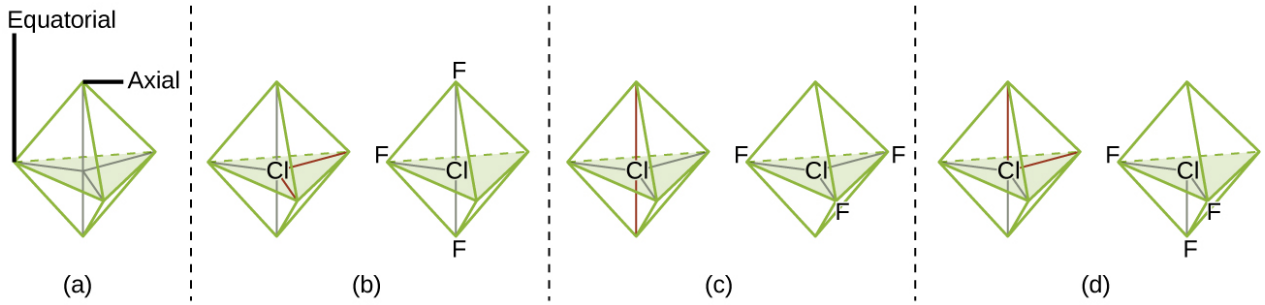


Figure **4.2.7**: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure **4.2.6**).

4.2.1.2: Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure **4.2.6**, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure **4.2.6**). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

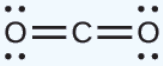
Example 4.2.1: Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

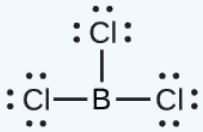
Solution

(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (Figure **4.2.8**).

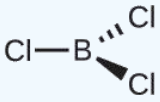


Figure **4.2.8**:

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

? Exercise 4.2.1

Carbonate, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

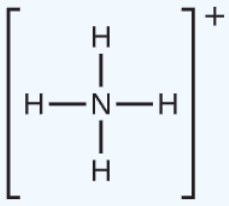
The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

✓ Example 4.2.2: Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the cation.

Solution

We write the Lewis structure of as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure **4.2.6**). Therefore, the electron pair geometry of Figure **4.2.9**.

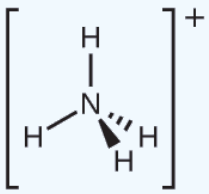


Figure **4.2.9**: The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Exercise 4.2.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

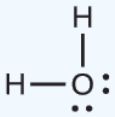
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 4.2.3: Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 4.2.10), as indicated in Figure 4.2.6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

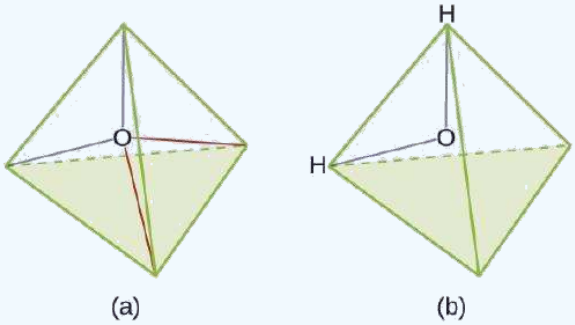


Figure 4.2.10: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 4.2.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

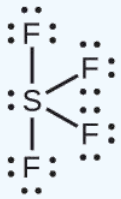
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 4.2.4: Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure **4.2.11**) is that of a seesaw (Figure **4.2.6**).

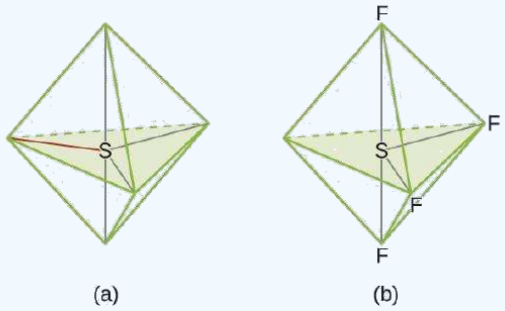


Figure **4.2.11**: (a) SF4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 4.2.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

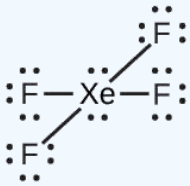
The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 4.2.5: Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure **4.2.6**), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure **4.2.12**). The five atoms are all in the same plane and have a square planar molecular structure.

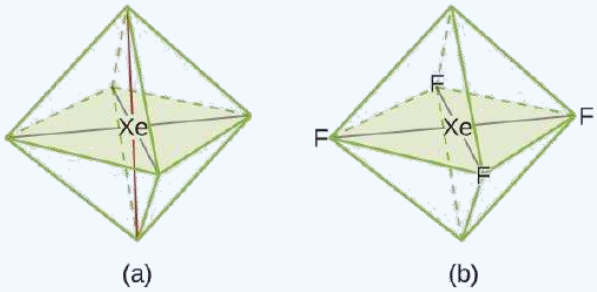


Figure **4.2.12**: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

? Exercise 4.2.5

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

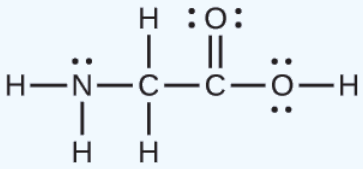
electron pair geometry: trigonal bipyramidal; molecular structure: linear

4.2.1.3: Molecular Structure for Multicenter Molecules

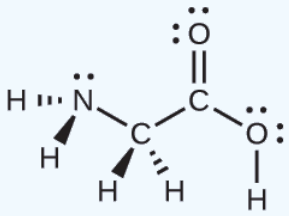
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

✓ Example 4.2.6: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

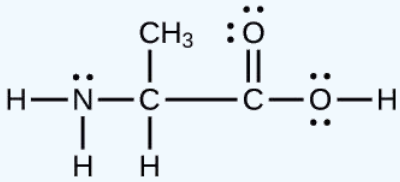
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

Exercise 4.2.6

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

Link to Learning

The molecular shape simulator lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example 4.2.7: Molecular Simulation

Using molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathbf{H{-}C{\equiv}N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 4.2.7

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

4.2.2: Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure **4.2.13**). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

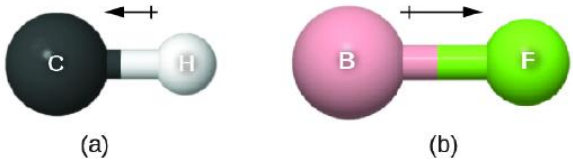


Figure **4.2.13**: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure **4.2.14**). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure **4.2.14**), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

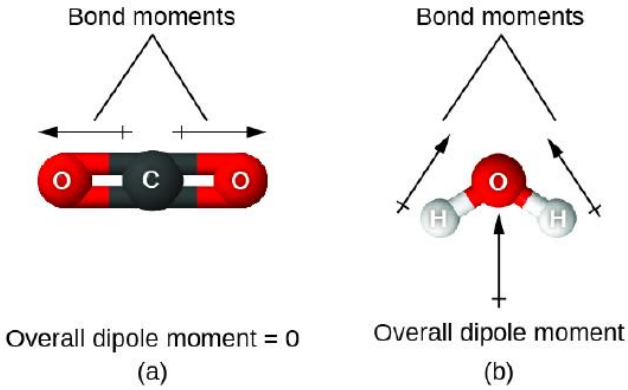
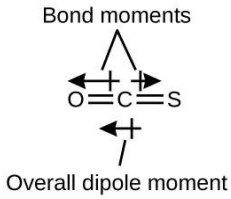


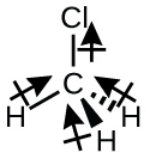
Figure **4.2.14**: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

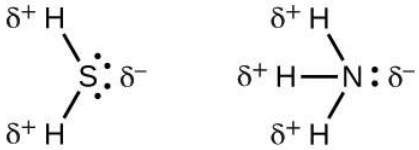


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

4.2.2.1: Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure **4.2.15**). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

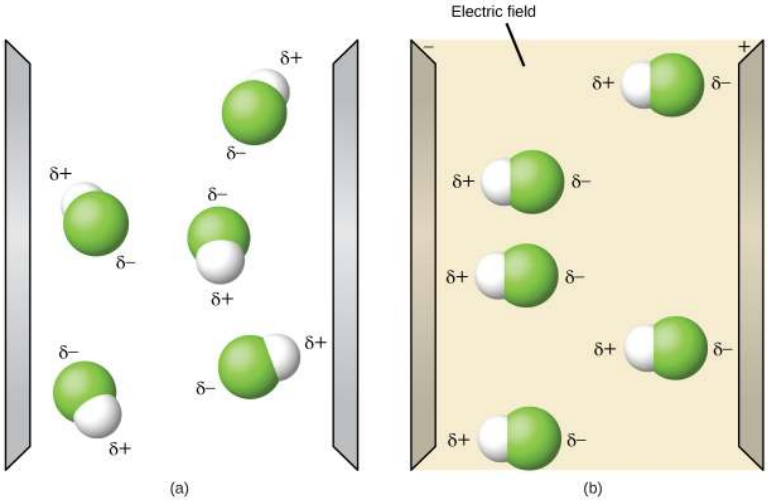


Figure **4.2.15**: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Link to Learning

The molecule polarity simulation provides many ways to explore dipole moments of bonds and molecules.

Example 4.2.8: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure **4.2.15**.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 4.2.8

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

This page titled 4.2: Molecular Structure and Polarity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **7.6: Molecular Structure and Polarity** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.3: Hybrid Atomic Orbitals

Learning Objectives

By the end of this section, you will be able to:

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1*s* orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure **4.3.1**, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

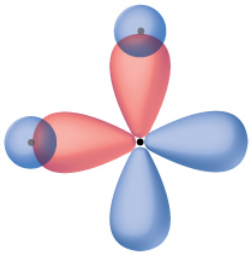


Figure **4.3.1**: The hypothetical overlap of two of the 2*p* orbitals on an oxygen atom (red) with the 1*s* orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1*s* orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure **4.3.2**). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

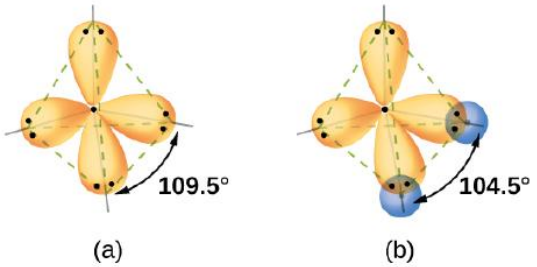


Figure **4.3.2**: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1*s* orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

4.3.1: *sp* Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent ***sp* hybrid orbitals** that are oriented in a linear geometry (Figure **4.3.3**). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

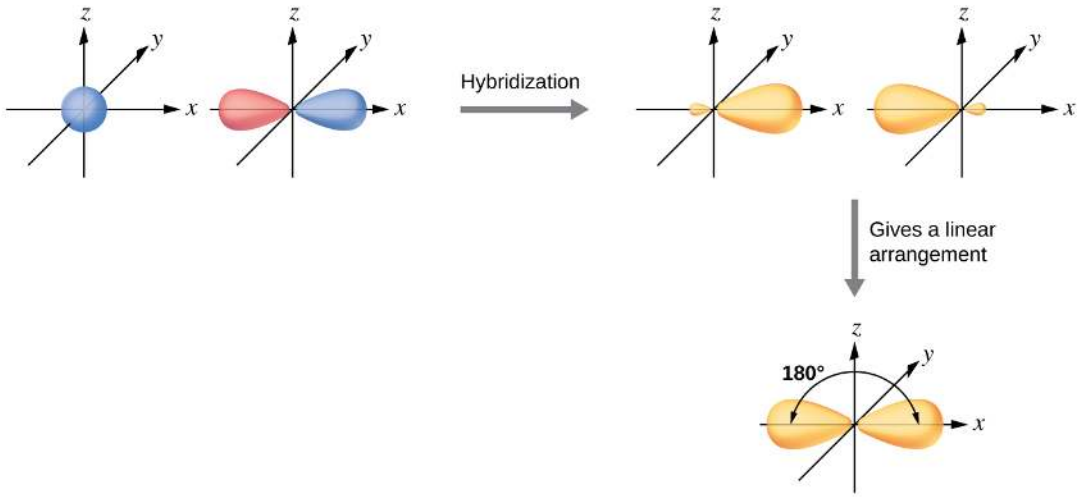


Figure **4.3.3**: Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure **4.3.4**. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

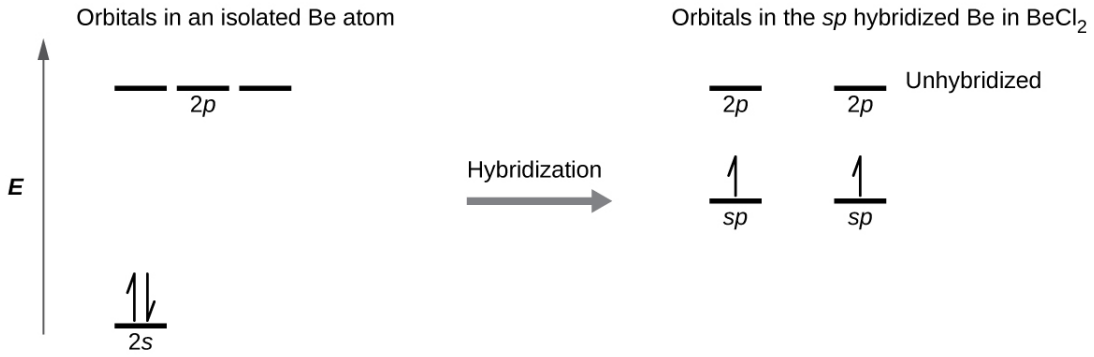


Figure **4.3.4**: This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

Link to Learning

Check out the University of Wisconsin-Oshkosh website to learn about visualizing hybrid orbitals in three dimensions.

4.3.2: sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three **sp^2 hybrid orbitals** and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one *s* orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure **4.3.5**).

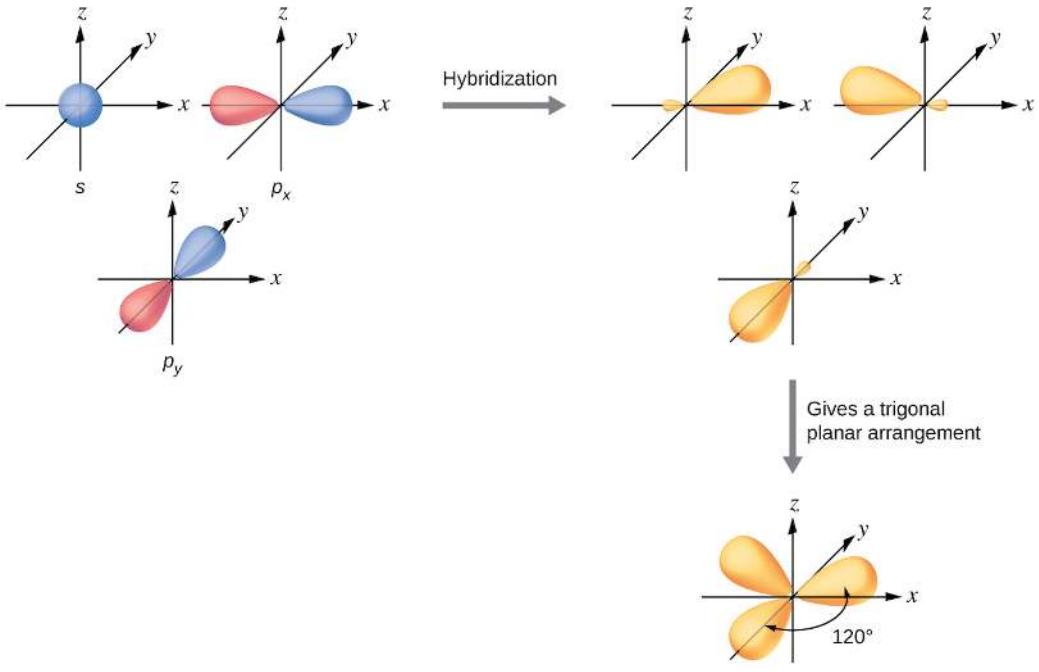


Figure **4.3.5**: The hybridization of an *s* orbital (blue) and two *p* orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure **4.3.5**, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure **4.3.6**, to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

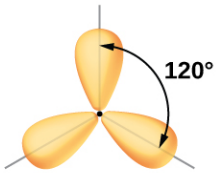


Figure **4.3.6**: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure **4.3.7**). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure **4.3.8**. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

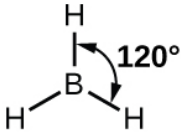


Figure **4.3.7**: BH_3 is an electron-deficient molecule with a trigonal planar structure.

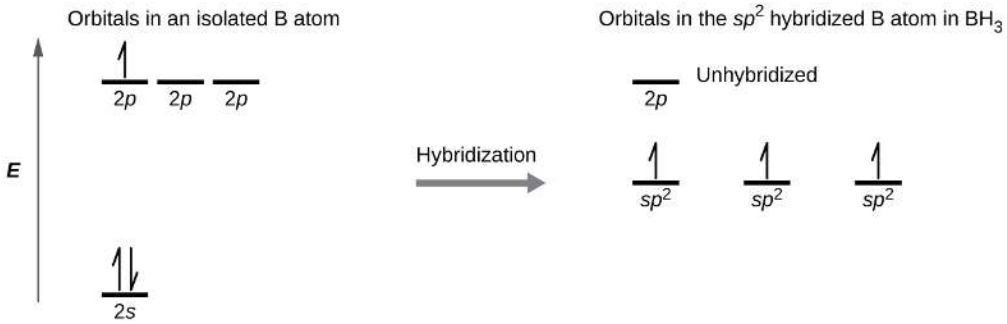


Figure **4.3.8**: In an isolated B atom, there are one 2*s* and three 2*p* valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2*p* orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure **4.3.9**), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

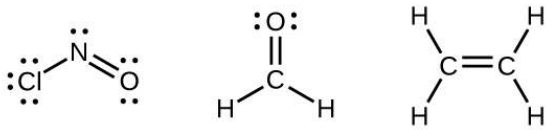


Figure **4.3.9**: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

4.3.3: sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four ***sp*^{3} hybrid orbitals**. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure **4.3.10**). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

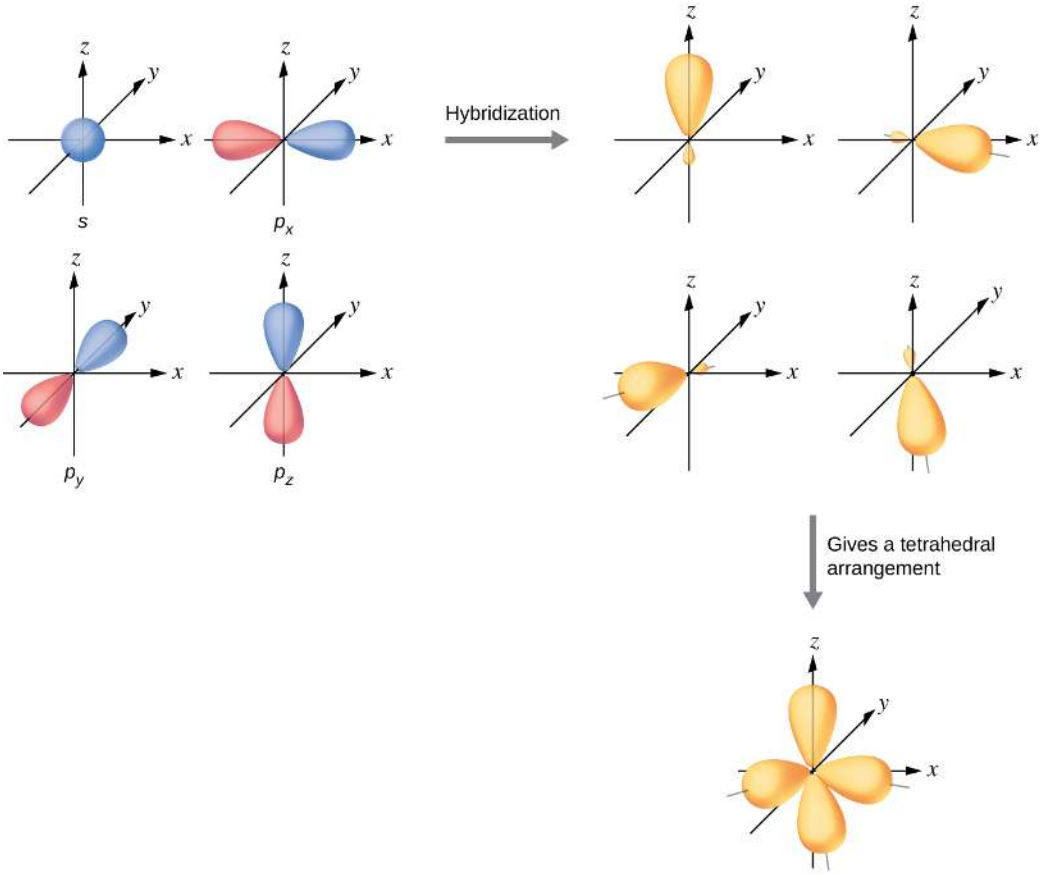


Figure **4.3.10**: The hybridization of an *s* orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure **4.3.11**. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

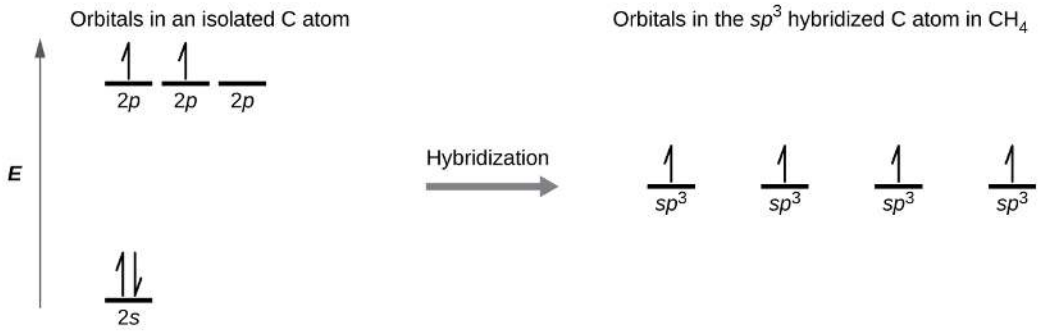


Figure **4.3.11**: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1*s* orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure **4.3.12**). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each

of the remaining sp^3 hybrid orbitals overlaps with an *s* orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure **4.3.12**. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

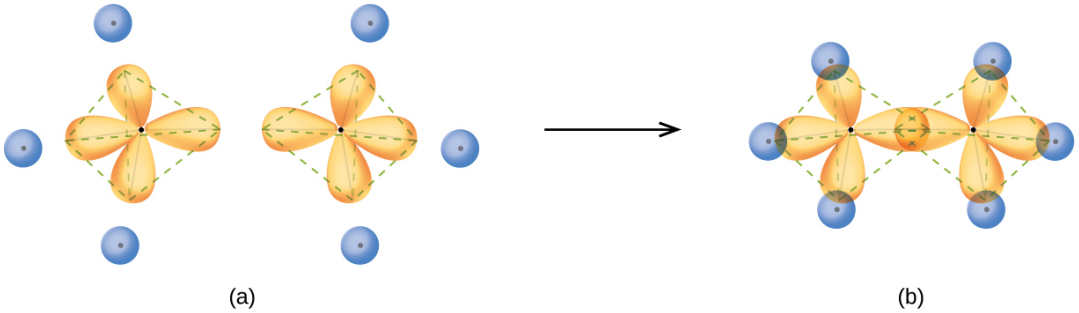


Figure **4.3.12**: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

4.3.4: sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five ***sp*^{3}*d* hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the *s* orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six ***sp*^{3}*d*^{2} hybrid orbitals**. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

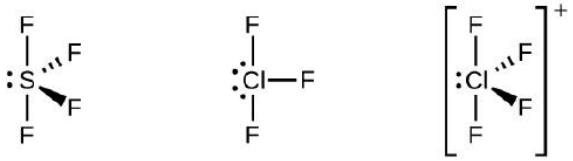


Figure **4.3.13**: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure **4.3.14**) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in (The electrons on fluorine atoms are omitted for clarity.)

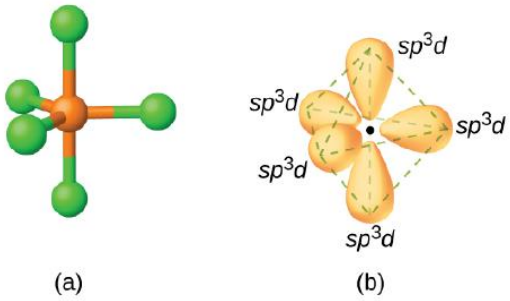


Figure **4.3.14**: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3*s* orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in the iodine atom in the interhalogens IF_5, and the xenon atom in XeF_4.

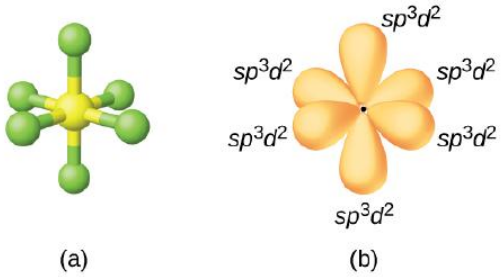


Figure **4.3.15**: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

4.3.5: Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure **4.3.16**. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure **4.3.16** that corresponds to this geometry.

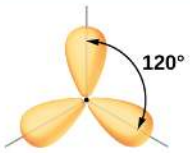
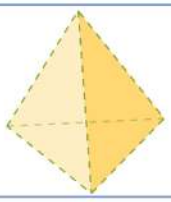
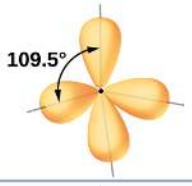
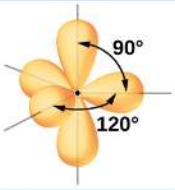
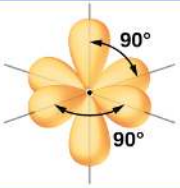
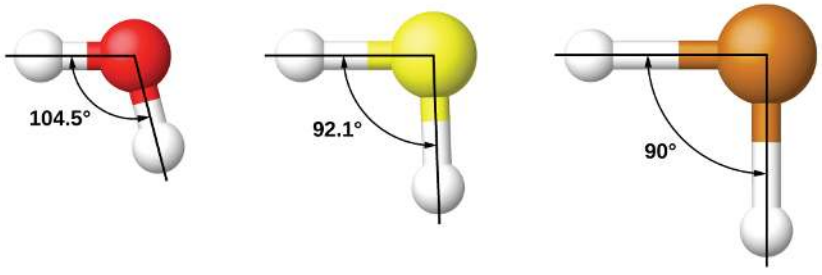
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure **4.3.16**: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

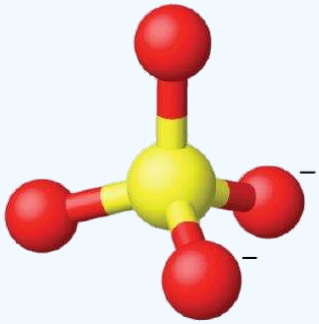


Example 4.3.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,

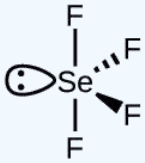
Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3.



Exercise 4.3.1

What is the hybridization of the selenium atom in SeF_4?



Answer

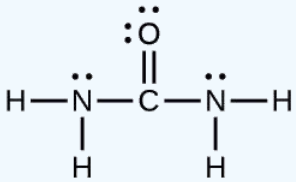
The selenium atom is sp^3d hybridized.

Example 4.3.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of the carbon atom in urea?

Solution

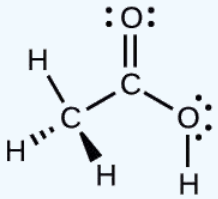
The Lewis structure of urea is



The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure **4.3.16**), which is the hybridization of the carbon atom in urea.

Exercise 4.3.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

4.3.6: Footnotes

- 1Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

This page titled 4.3: Hybrid Atomic Orbitals is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **8.2: Hybrid Atomic Orbitals** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

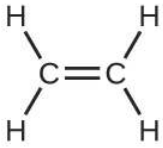
4.3.1: Extra-Multiple Bonds

Learning Objectives

By the end of this section, you will be able to:

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the 2*p* orbitals and the 2*s* orbital (Figure **4.3.1.1**).

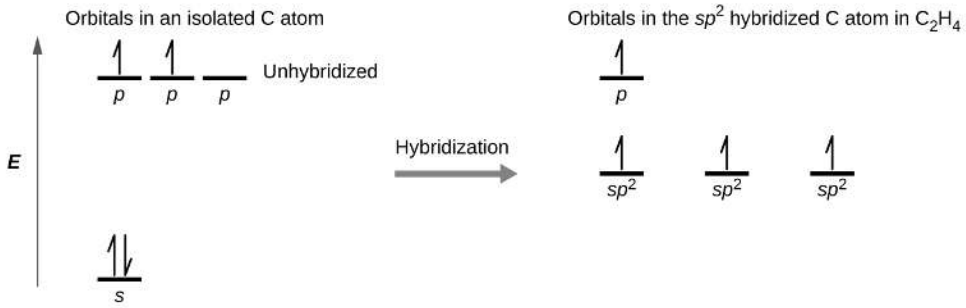


Figure **4.3.1.1**: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the *p* orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

These orbitals form the C–H single bonds and the σ bond in the Figure **4.3.1.2**. The π bond in the C=C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure **4.3.1.2**) is perpendicular to the plane of the sp2 hybrid orbitals. Thus the unhybridized 2p orbitals overlap in a side-by-side fashion, above and below the internuclear axis (Figure **4.3.1.2**) and form a π bond.

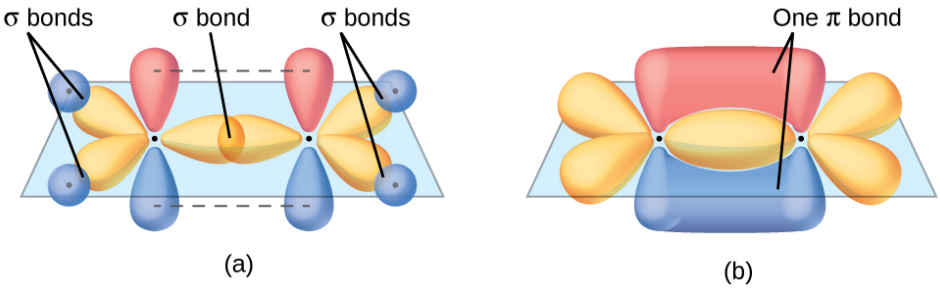


Figure **4.3.1.2**: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with *s* orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the *p* orbitals would not be oriented to overlap efficiently to create the π bond. The planar

configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom (Figure **4.3.1.3**). We find this situation in acetylene, **H–C≡C–H** (Figure **4.3.1.4**), The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

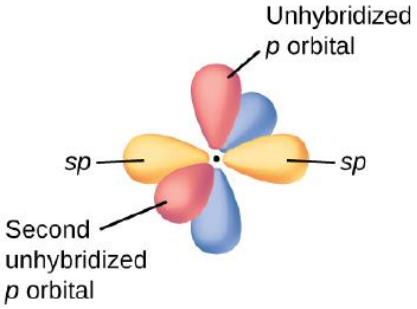


Figure **4.3.1.3**: Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized *p* orbitals at perpendicular angles.

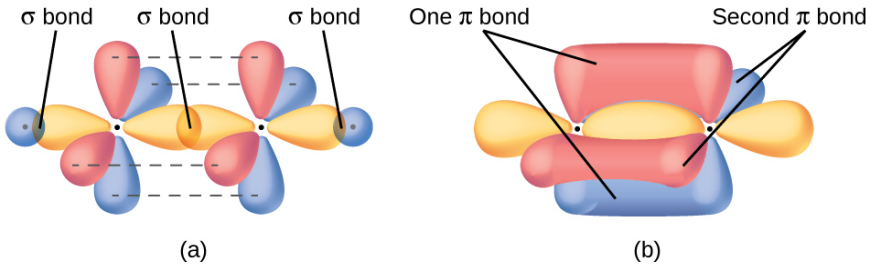


Figure **4.3.1.4**: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure **4.3.1.5**). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)

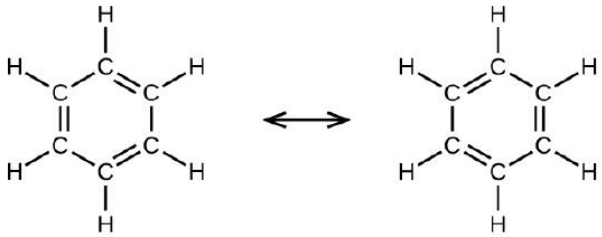


Figure **4.3.1.5**: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.

Example 4.3.1.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are



The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

Exercise 4.3.1.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

This page titled 4.3.1: Extra-Multiple Bonds is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **8.3: Multiple Bonds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.4: Intermolecular Forces

Learning Objectives

By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure **4.4.1** illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

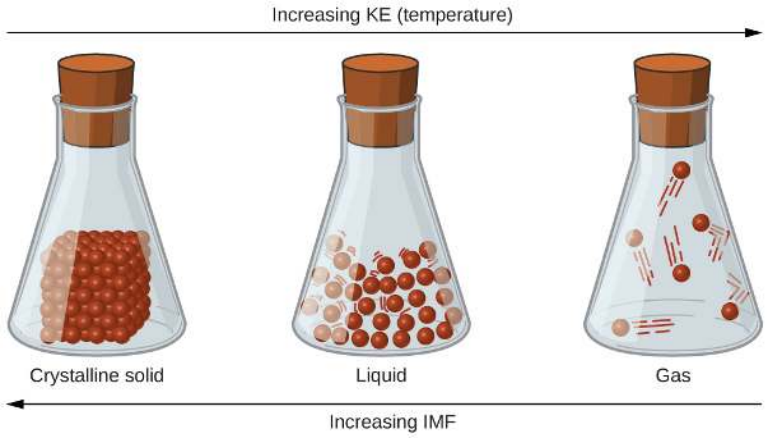


Figure **4.4.1**: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure **4.4.2**.



Figure **4.4.2**: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure **4.4.3**.



Figure **4.4.3**: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Link to Learning

Access this interactive simulation on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

4.4.1: Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure **4.4.4**: illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

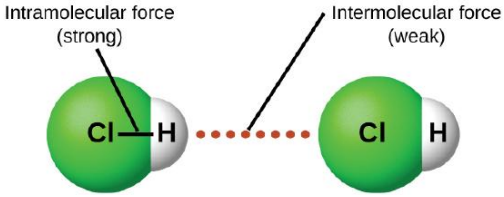


Figure 4.4.4: *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

4.4.2: Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 4.4.5.

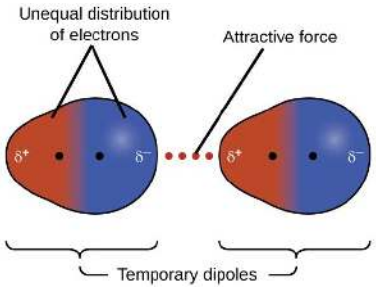


Figure 4.4.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 4.4.1.

Table 4.4.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more

easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

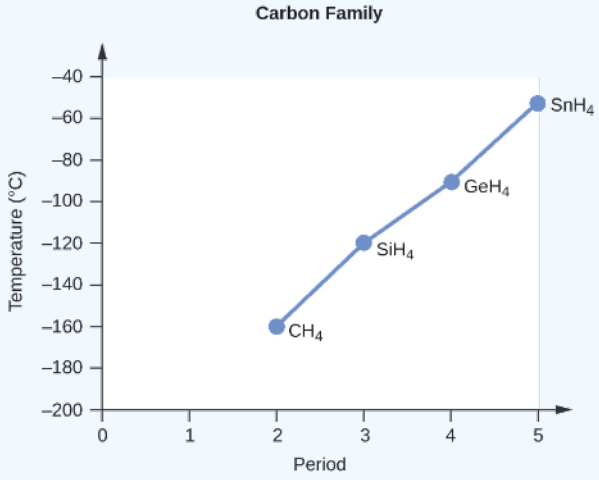
Example 4.4.1: London Forces and Their Effects

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:



Exercise 4.4.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

$C_2H_6 < C_3H_8 < C_4H_{10}$. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $C_2H_6 < C_3H_8 < C_4H_{10}$.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure **4.4.6**) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for

intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

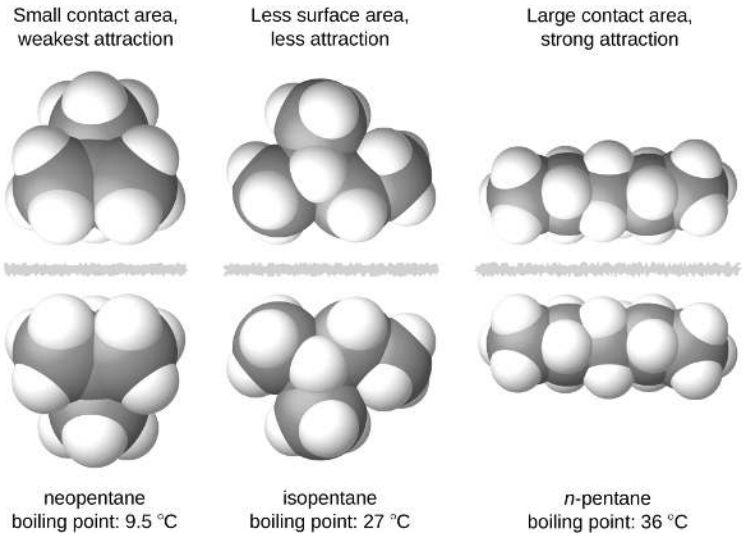


Figure **4.4.6**: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Chemistry in Everyday Life: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure **4.4.7**, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Later research led by Alyssa Stark at University of Akron showed that geckos can maintain their hold on hydrophobic surfaces (similar to the leaves in their habitats) equally well whether the surfaces were wet or dry. Stark's experiment used a ribbon to gently pull the geckos until they slipped, so that the researchers could determine the geckos' ability to hold various surfaces under wet and dry conditions. Further investigations may eventually lead to the development of better adhesives and other applications.

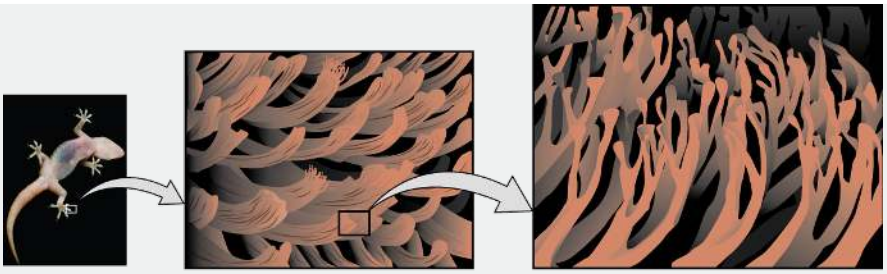


Figure 4.4.7: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Link to Learning

Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

4.4.3: Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 4.4.8.

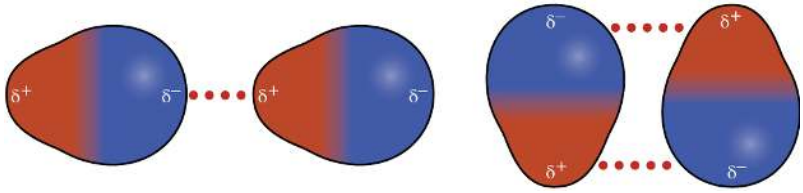


Figure 4.4.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 4.4.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit

dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

? Exercise 4.4.2

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

4.4.4: Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the hydrogen bonds are denoted by dots. Figure **4.4.9** illustrates hydrogen bonding between water molecules.

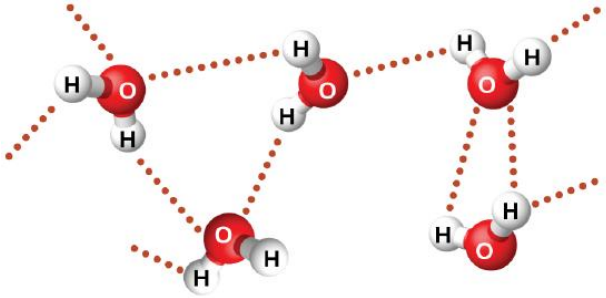


Figure **4.4.9**: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure **4.4.10**. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

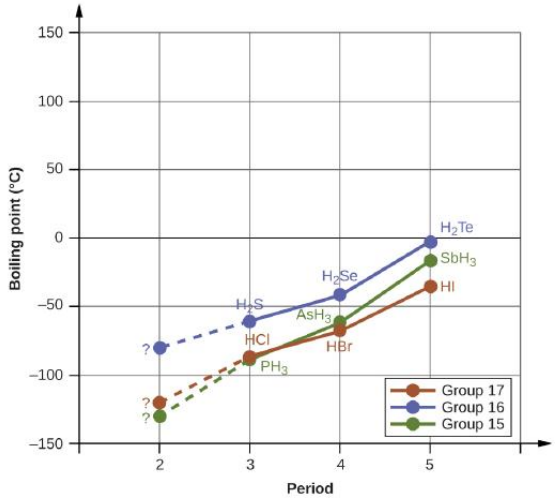


Figure **4.4.10**: For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure **4.4.11**. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

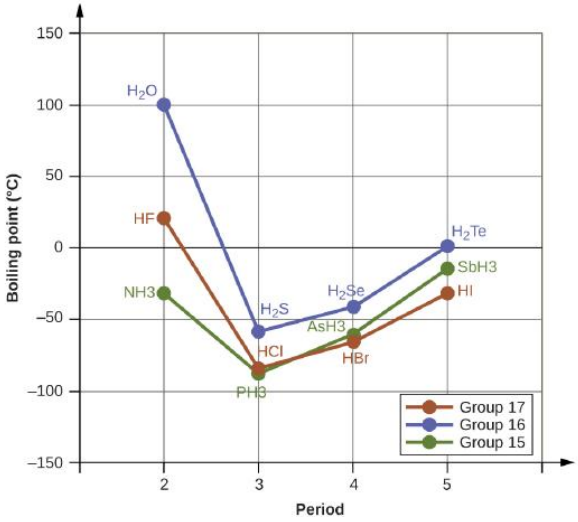


Figure **4.4.11**: In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

✔ Example 4.4.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$.

https://chem.libretexts.org/@go/page/432935

The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 4.4.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

How Sciences Interconnect: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 4.4.12.

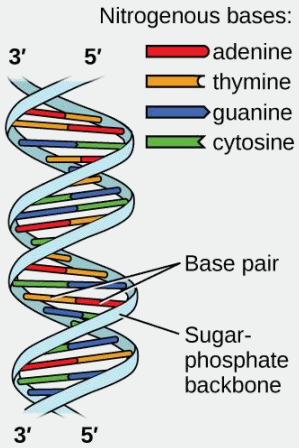


Figure 4.4.12: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 4.4.13.

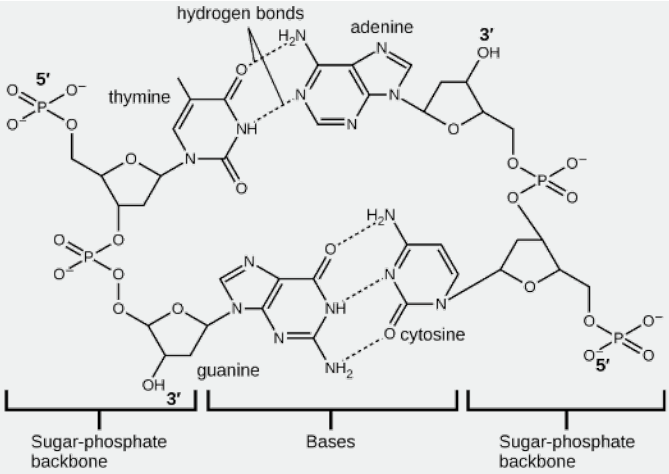


Figure **4.4.13**: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

This page titled 4.4: Intermolecular Forces is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **10.1: Intermolecular Forces** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.4.1: Extra-Properties of Liquids

Learning Objectives

By the end of this section, you will be able to:

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure **4.4.1.1**, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).

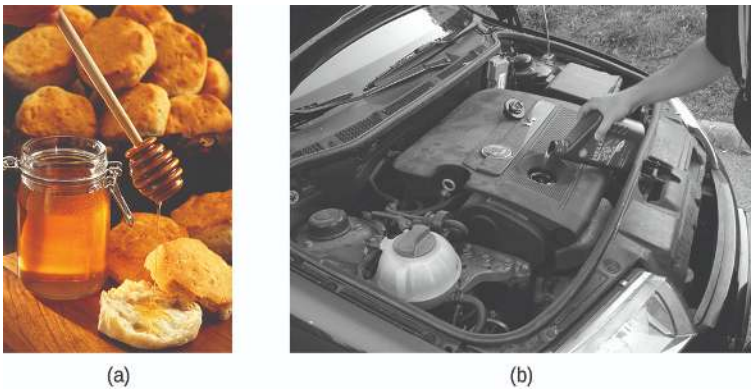


Figure **4.4.1.1**: (a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table **4.4.1.1** shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Table **4.4.1.1**: Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of cohesive forces. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the

molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure **4.4.1.2**, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

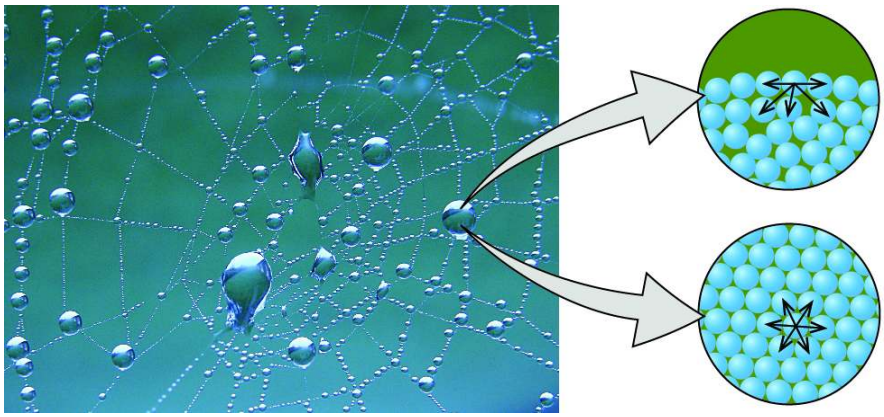


Figure **4.4.1.2**: Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table **4.4.1.2**. Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure **4.4.1.3**, even though they are denser than water, move on its surface because they are supported by the surface tension.

Table **4.4.1.2**: Surface Tensions of Common Substances at 25 °C

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

Surface tension is affected by a variety of variables, including the introduction of additional substances on the surface. In the late 1800s, Agnes Pockels, who was initially blocked from pursuing a scientific career but studied on her own, began investigating the impact and characteristics of soapy and greasy films in water. Using homemade materials, she developed an instrument known as a trough for measuring surface contaminants and their effects. With the support of renowned scientist Lord Rayleigh, her 1891 paper showed that surface contamination significantly reduces surface tension, and also that changing the characteristics of the surface (compressing or expanding it) also affects surface tension. Decades later, Irving Langmuir and Katharine Blodgett built on Pockels' work in their own trough and important advances in surface chemistry. Langmuir pioneered methods for producing single-molecule layers of film; Blodgett applied these to the development of non-reflective glass (critical for film-making and other applications), and also studied methods related to cleaning surfaces, which are important in semiconductor fabrication.

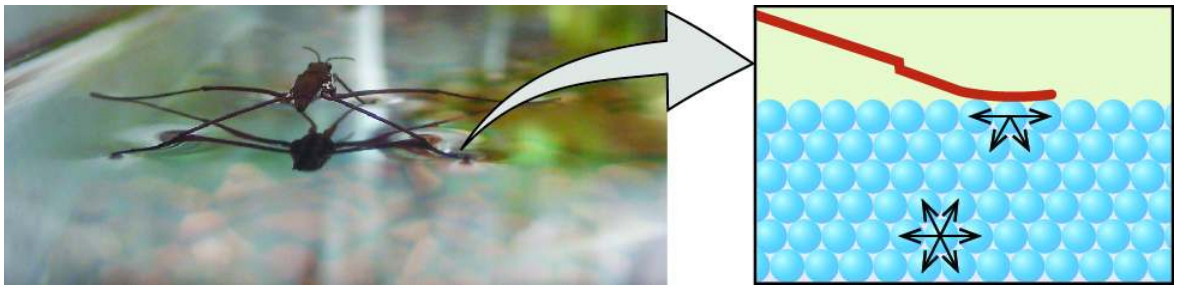


Figure 4.4.1.3: Surface tension (right) prevents this insect, a “water strider,” from sinking into the water.

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not “wet” the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure 4.4.1.4).

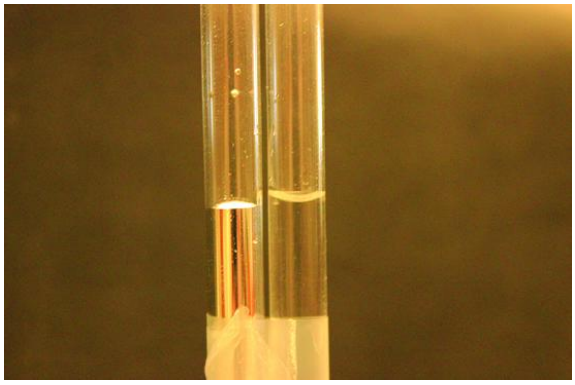


Figure 4.4.1.4: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

If you place one end of a paper towel in spilled wine, as shown in Figure 4.4.1.5, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.

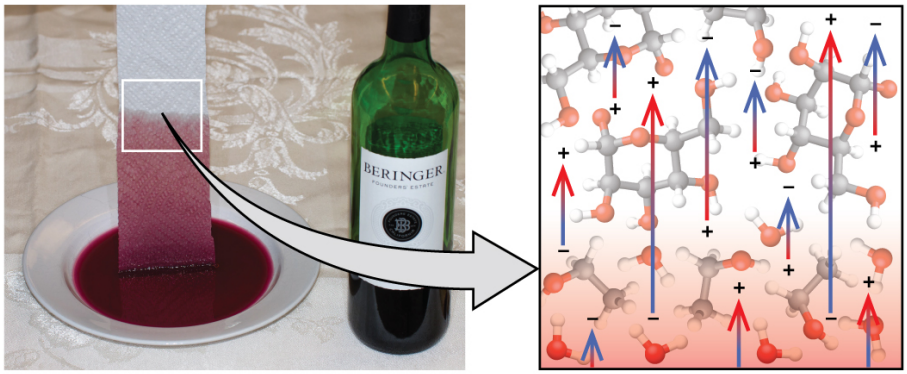


Figure 4.4.1.5: Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the −OH groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many −OH groups. Water molecules are attracted to these −OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure 4.4.1.6. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.

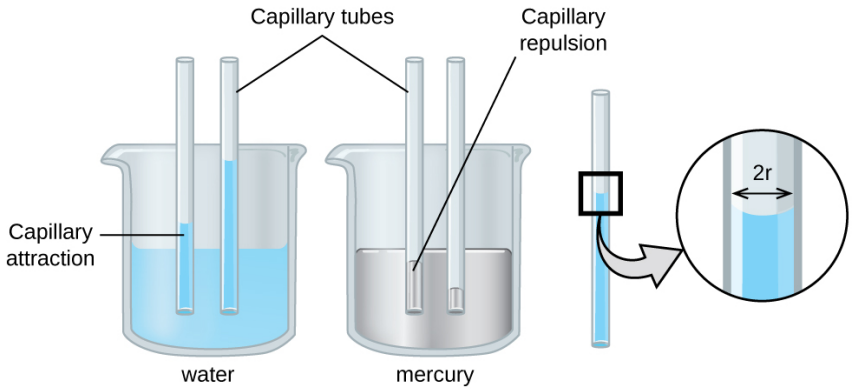


Figure 4.4.1.6: Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T\cos\theta}{r\rho g} \tag{4.4.1.1}$$

In this equation, h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube, T is the surface tension of the liquid, θ is the contact angle between the liquid and the tube, r is the radius of the tube, ρ is the density of the

liquid, and g is the acceleration due to gravity, 9.8 m/s^2. When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube.

Example 4.4.1.1: Capillary Rise

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm?

For water, T = 71.99 mN/m and ρ = 1.0 g/cm^3.

Solution

The liquid will rise to a height h given by Equation 4.4.1.1:

$$h = \frac{2T\cos\theta}{r\rho g}$$

The Newton is defined as a kg m/s^2, and so the provided surface tension is equivalent to 0.07199 kg/s^2. The provided density must be converted into units that will cancel appropriately: ρ = 1000 kg/m^3. The diameter of the tube in meters is 0.00025 m, so the radius is 0.000125 m. For a glass tube immersed in water, the contact angle is θ = 0°, so cos θ = 1. Finally, acceleration due to gravity on the earth is g = 9.8 m/s^2. Substituting these values into the equation, and cancelling units, we have:

$$h = \frac{2\left(0.07199 kg/s^2\right)}{\left(0.000125 m\right)\left(1000 kg/m^3\right)\left(9.8 m/s^2\right)} = 0.12 m = 12 cm$$

Exercise 4.4.1.1

Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

Answer

diameter = 0.36 mm

Chemistry in Everyday Life: Biomedical Applications of Capillary Action

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in Figure 4.4.1.7. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.



Figure **4.4.1.7**: Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

This page titled 4.4.1: Extra-Properties of Liquids is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **10.2: Properties of Liquids** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

4.5: Exercises (Lewis Structures)

1.

Does a cation gain protons to form a positive charge or does it lose electrons?

2.

Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and SO_4^{2}msup ions. Explain why a sample of iron(III) sulfate is uncharged.

3.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

4.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

5.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

6.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

7.

Write the electron configuration for each of the following ions:

(a) As^{3-}

(b) I^{-}

(c) Be^{2+}

(d) Cd^{2+}

(e) O^{2-}

(f) Ga^{3+}

(g) Li^{+}

(h) N^{3-}

(i) Sn^{2+}

(j) Co^{2+}

(k) Fe^{2+}

(l) As^{3+}

8.

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

9.

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

(a) Al

(b) Br

(c) Sr

(d) Li

(e) As

(f) S

10.

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

11.

Why is it incorrect to speak of a molecule of solid NaCl?

12.

What information can you use to predict whether a bond between two atoms is covalent or ionic?

13.

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a) Cl_2CO

(b) MnO

(c) NCl_3

(d) $CoBr_2$

(e) K_2S

(f) CO

(g) CaF_2

(h) HI

(i) CaO

(j) IBr

(k) CO_2

14.

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

15.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

16.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) N or P

(b) N or Ge

(c) S or F

(d) Cl or S

(e) H or C

(f) Se or P

(g) C or Si

17.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O

(b) Br, Cl, F, H, I

(c) F, H, O, P, S

(d) Al, H, Na, O, P

(e) Ba, H, N, O, As

18.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) As, H, N, P, Sb

(b) Cl, H, P, S, Si

(c) Br, Cl, Ge, H, Sr

(d) Ca, H, K, N, Si

(e) Cl, Cs, Ge, H, Sr

19.

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

20.

Which is the most polar bond?

(a) C–C

(b) C–H

(c) N–H

(d) O–H

(e) Se–H

21.

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

22.

Which of the following molecules or ions contain polar bonds?

(a) O_3

(b) S_8

(c) $\mathbf{O_2^{2-}}$

(d) $\mathbf{NO_3^-}$

(e) CO_2

(f) H_2S

(g) $\mathbf{BH_4^-}$

23.

Name the following compounds:

(a) CsCl

(b) BaO

(c) K_2S

(d) $BeCl_2$

(e) HBr

(f) AlF_3

24.

Name the following compounds:

(a) NaF

(b) Rb_2O

(c) BCl_3

(d) H_2Se

(e) P_4O_6

(f) ICl_3

25.

Write the formulas of the following compounds:

(a) rubidium bromide

(b) magnesium selenide

(c) sodium oxide

(d) calcium chloride

(e) hydrogen fluoride

(f) gallium phosphide

(g) aluminum bromide

(h) ammonium sulfate

26.

Write the formulas of the following compounds:

(a) lithium carbonate

(b) sodium perchlorate

(c) barium hydroxide

(d) ammonium carbonate

(e) sulfuric acid

(f) calcium acetate

(g) magnesium phosphate

(h) sodium sulfite

27.

Write the formulas of the following compounds:

(a) chlorine dioxide

(b) dinitrogen tetraoxide

(c) potassium phosphide

(d) silver(I) sulfide

(e) aluminum fluoride trihydrate

(f) silicon dioxide

28.

Write the formulas of the following compounds:

(a) barium chloride

(b) magnesium nitride

(c) sulfur dioxide

(d) nitrogen trichloride

(e) dinitrogen trioxide

(f) tin(IV) chloride

29.

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) Cr_2O_3

(b) $FeCl_2$

(c) CrO_3

(d) $TiCl_4$

(e) $CoCl_2 \cdot 6H_2O$

(f) MoS_2

30.

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) $NiCO_3$

(b) MoO_3

(c) $Co(NO_3)_2$

(d) V_2O_5

(e) MnO_2

(f) Fe_2O_3

31.

The following ionic compounds are found in common household products. Write the formulas for each compound:

(a) potassium phosphate

(b) copper(II) sulfate

(c) calcium chloride

(d) titanium(IV) oxide

(e) ammonium nitrate

(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

32.

The following ionic compounds are found in common household products. Name each of the compounds:

(a) $Ca(H_2PO_4)_2$

(b) $FeSO_4$

(c) $CaCO_3$

(d) MgO

(e) $NaNO_2$

(f) KI

33.

What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$Fe(NO_3)_3$]

(d) titanium tetrachloride

(e) cupric bromide ($CuBr_2$)

34.

Write the Lewis symbols for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) O^{2-}

(e) Ga^{3+}

(f) Li^+

(g) N^{3-}

35.

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

36.

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al_2O_3

(c) $GaCl_3$

(d) K_2O

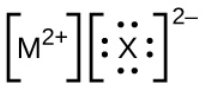
(e) Li_3N

(f) KF

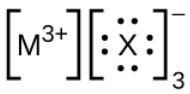
37.

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

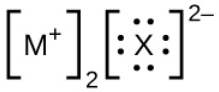
(a)



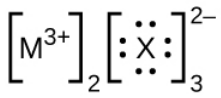
(b)



(c)



(d)



38.

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

39.

Write Lewis structures for the following:

(a) H_2

(b) HBr

(c) PCl_3

(d) SF_2

(e) H_2CCH_2

(f) HNNH

(g) H_2CNH

(h) NO^-

(i) N_2

(j) CO

(k) CN^-

40.

Write Lewis structures for the following:

(a) O_2

(b) H_2CO

(c) AsF_3

(d) ClNO

(e) $SiCl_4$

(f) H_3O^+

(g) $\mathbf{NH_4^+}$

(h) $\mathbf{BF_4^-}$

(i) HCCH

(j) ClCN

(k) $\mathbf{C_2^{2+}}$

41.

Write Lewis structures for the following:

(a) ClF_3

(b) PCl_5

(c) BF_3

(d) $\mathbf{PF_6^-}$

42.

Write Lewis structures for the following:

(a) SeF_6

(b) XeF_4

(c) $\mathbf{SeCl_3^+}$

(d) Cl_2BBCl_2 (contains a B–B bond)

43.

Write Lewis structures for:

(a) $\mathbf{PO_4^{3-}}$

(b) $\mathbf{ICl_4^-}$

(c) $\mathbf{SO_3^{2-}}$

(d) HONO

44.

Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

45.

Write Lewis structures for the following molecules or ions:

(a) SbH_3

(b) XeF_2

(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

46.

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

47.

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

48.

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

49.

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

(a) $1s^2 2s^2 2p^5$

(b) $1s^2 2s^2 2p^6 3s^2$

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

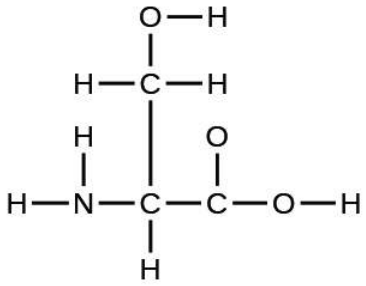
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

(e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

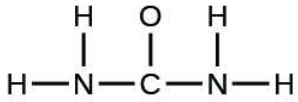
50.

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

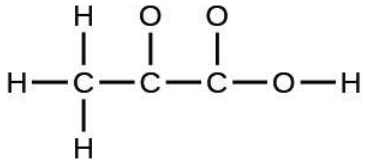
(a) the amino acid serine:



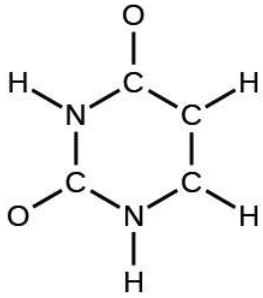
(b) urea:



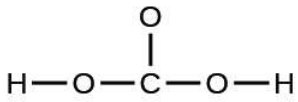
(c) pyruvic acid:



(d) uracil:



(e) carbonic acid:



51.

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

52.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

53.

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

54.

How are single, double, and triple bonds similar? How do they differ?

55.

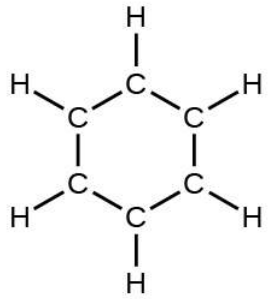
Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) selenium dioxide, OSeO

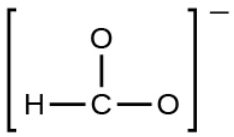
(b) nitrate ion, $\mathbf{NO_3^-}$

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)

(d) benzene, C_6H_6:



(e) the formate ion:



56.

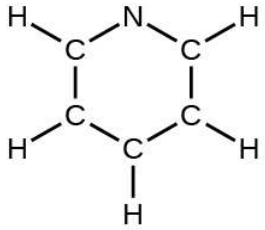
Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) sulfur dioxide, SO_2

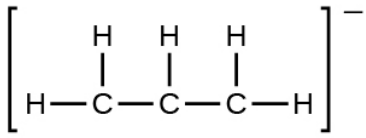
(b) carbonate ion, $\mathbf{CO_3^{2-}}$

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:



(e) the allyl ion:



57.

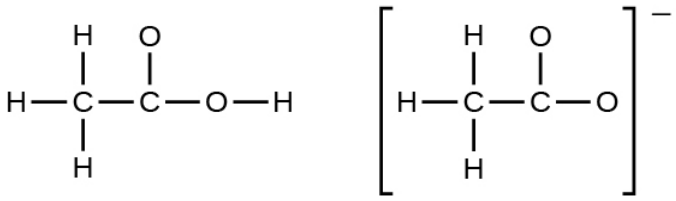
Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

58.

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-.

59.

In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



60.

Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

(a) CO_2

(b) CO

61.

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

62.

Determine the formal charge of each element in the following:

(a) HCl

(b) CF_4

(c) PCl_3

(d) PF_5

63.

Determine the formal charge of each element in the following:

(a) H_3O^+

(b) $\mathbf{SO_4^{2-}}$

(c) NH_3

(d) $\mathbf{O_2^{2-}}$

(e) H_2O_2

64.

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

65.

Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO

(b) NO^-

(c) $\mathbf{BF_4^-}$

(d) $\mathbf{SnCl_3^-}$

(e) H_2CCH_2

(f) ClF_3

(g) SeF_6

(h) $\mathbf{PO_4^{3-}}$

66.

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

(a) O_3

(b) SO_2

(c) $\mathbf{NO_2^-}$

(d) $\mathbf{NO_3^-}$

67.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

68.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

69.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

70.

Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

71.

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

(a) IF

(b) IF_3

(c) IF_5

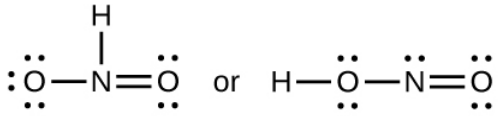
(d) IF_7

72.

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

73.

Which of the following structures would we expect for nitrous acid? Determine the formal charges:



74.

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.

75.

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

76.

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

77.

Explain the difference between electron-pair geometry and molecular structure.

78.

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

79.

Explain how a molecule that contains polar bonds can be nonpolar.

80.

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

81.

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6

(b) PCl_5

(c) BeH_2

(d) CH_3^+

82.

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) IF_6^+

(b) CF_4

(c) BF_3

(d) SiF_5^-

(e) $BeCl_2$

83.

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2-}$

(d) PCl_3

(e) SeF_4

(f) PH_2^-

84.

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^+$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

85.

Identify the electron pair geometry and the molecular structure of each of the following molecules:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

86.

Predict the electron pair geometry and the molecular structure of each of the following:

(a) IOF_5 (I is the central atom)

(b) $POCl_3$ (P is the central atom)

(c) Cl_2SeO (Se is the central atom)

(d) $ClSO^+$ (S is the central atom)

(e) F_2SO (S is the central atom)

(f) NO_2^-

(g) SiO_4^{4-}

87.

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2-}$

(d) PCl_3

(e) SeF_4

(f) PH_2^-

(g) XeF_2

88.

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^-$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

89.

Which of the following molecules have dipole moments?

(a) CS_2

(b) SeS_2

(c) CCl_2F_2

(d) PCl_3 (P is the central atom)

(e) ClNO (N is the central atom)

90.

Identify the molecules with a dipole moment:

(a) SF_4

(b) CF_4

(c) Cl_2CCBr_2

(d) CH_3Cl

(e) H_2CO

91.

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

92.

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

93.

Is the Cl_2BBCl_2 molecule polar or nonpolar?

94.

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

95.

Describe the molecular structure around the indicated atom or atoms:

(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]

(b) the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]

(c) the oxygen atom in hydrogen peroxide, HOOH

(d) the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]

(e) the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]

(f) the central oxygen atom in the ozone molecule, O_3

(g) each of the carbon atoms in propyne, CH_3CCH

(h) the carbon atom in Freon, CCl_2F_2

(i) each of the carbon atoms in allene, H_2CCCH_2

96.

Draw the Lewis structures and predict the shape of each compound or ion:

(a) CO_2

(b) NO_2^-

(c) SO_3

(d) SO_3^{2-}

97.

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

98.

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

99.

Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

(a) CS_3^{2-}

(b) CS_2

(c) CS

(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

100.

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

101.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

102.

Use the simulation to perform the following exercises for a two-atom molecule:

(a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.

(b) With a partial positive charge on A, turn on the electric field and describe what happens.

(c) With a small partial negative charge on A, turn on the electric field and describe what happens.

(d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

103.

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

(a) Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.

(b) Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

104.

Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

105.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the “real” and “model” modes. Explain the difference observed.

106.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O. What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

This page titled 4.5: Exercises (Lewis Structures) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

4.5.1: Answers to Selected Exercises

1.

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

3.

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

5.

(a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

7.

(a) [Ar]$4s^2 3d^{10} 4p^6$; (b) [Kr]$4d^{10} 5s^2 5p^6$ (c) $1s^2$ (d) [Kr]$4d^{10}$; (e) [He]$2s^2 2p^6$; (f) [Ar]$3d^{10}$; (g) $1s^2$ (h) [He]$2s^2 2p^6$ (i) [Kr]$4d^{10} 5s^2$ (j) [Ar]$3d^7$ (k) [Ar]$3d^6$, (l) [Ar]$3d^{10} 4s^2$

9.

(a) $1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+}: $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$; Sr^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (d) $1s^2 2s^1$; Li^{+}: $1s^2$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (f) $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

11.

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

13.

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

15.

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

17.

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

19.

N, O, F, and Cl

21.

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

23.

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

25.

(a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

27.

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) $AIF_3 \cdot 3H_2O$; (f) SiO_2

29.

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) chloride hexahydrate; (f) molybdenum(IV) sulfide

31.

(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

33.

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

34.

(a) eight electrons:



(b) eight electrons:



(c) no electrons Be^{2+}

(d) eight electrons:



(e) no electrons Ga^{3+}

(f) no electrons Li^{+}

(g) eight electrons:



36.

(a)

Mg^{2+} 

(b)

Al^{3+} 

(c)

Ga^{3+} 

(d)

K^{+} 

(e)

Li^{+} 

(f)

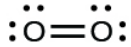
K^{+} 

38.



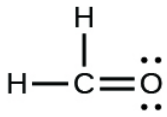
40.

(a)

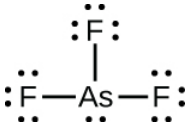


In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

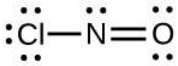
(b)



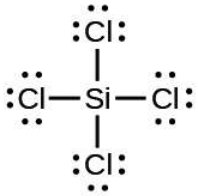
(c)



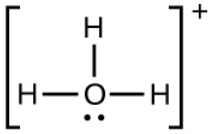
(d)



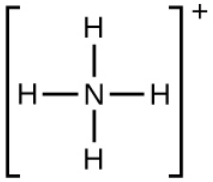
(e)



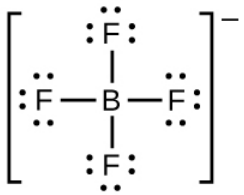
(f)



(g)



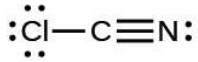
(h)



(i)



(j)

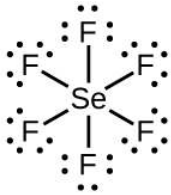


(k)

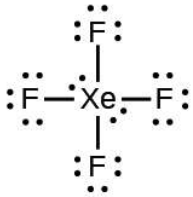


42.

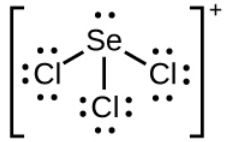
(a) SeF_6:



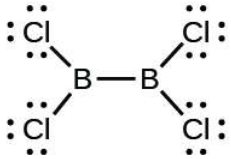
(b) XeF_4:



(c) $SeCl_3^+$:



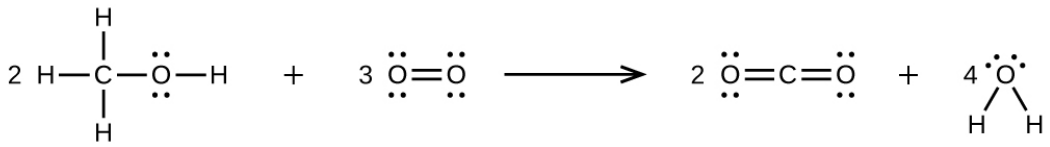
(d) Cl_2BBCl_2:

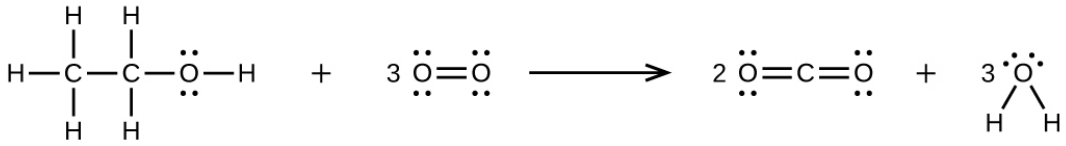


44.

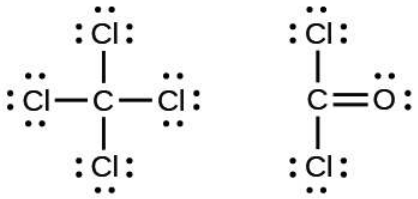
Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

46.



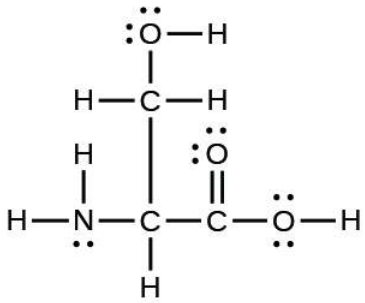


48.

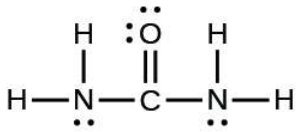


50.

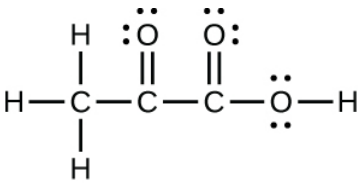
(a)



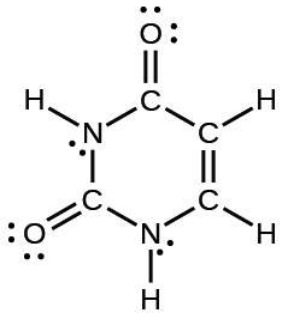
(b)



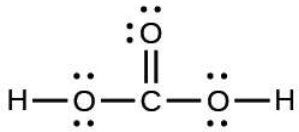
(c)



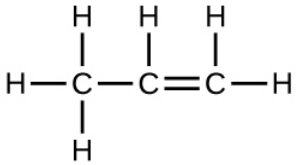
(d)



(e)



52.

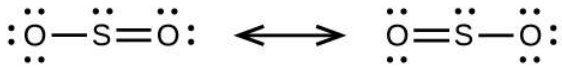


54.

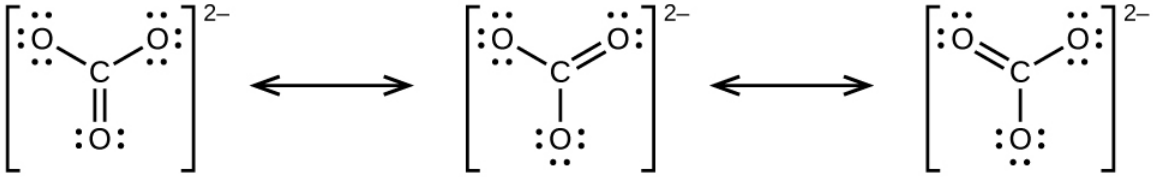
Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

56.

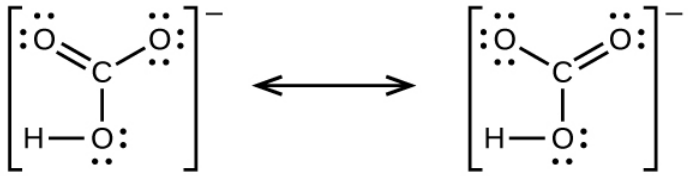
(a)



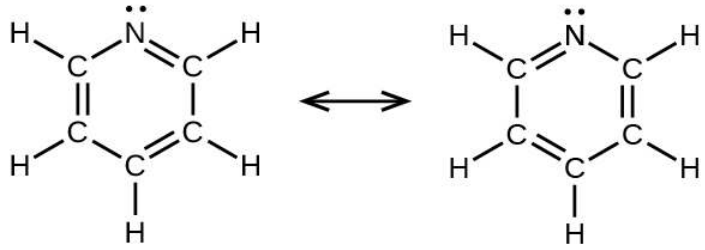
(b)



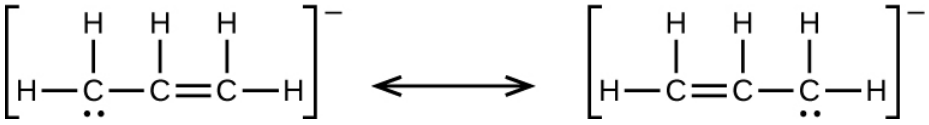
(c)



(d)

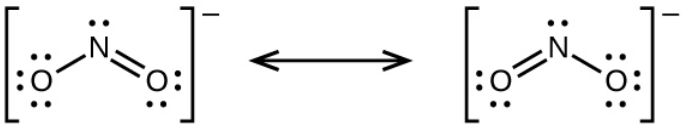


(e)



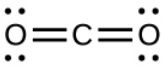
58.

For NO_2^-



60.

(a)



(b)



CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

62.

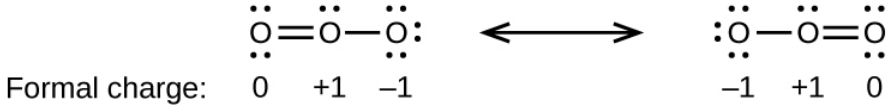
(a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl 0; (d) P: 0, F: 0

64.

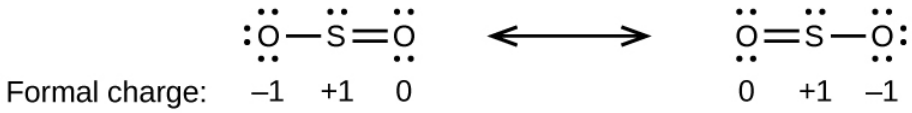
Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

66.

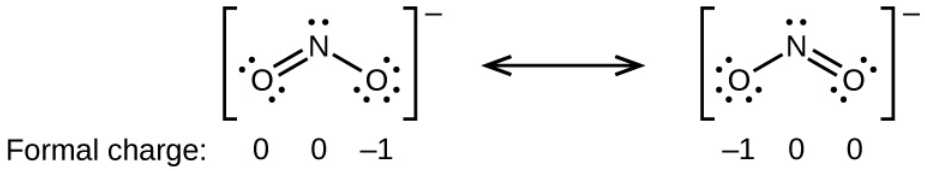
(a)



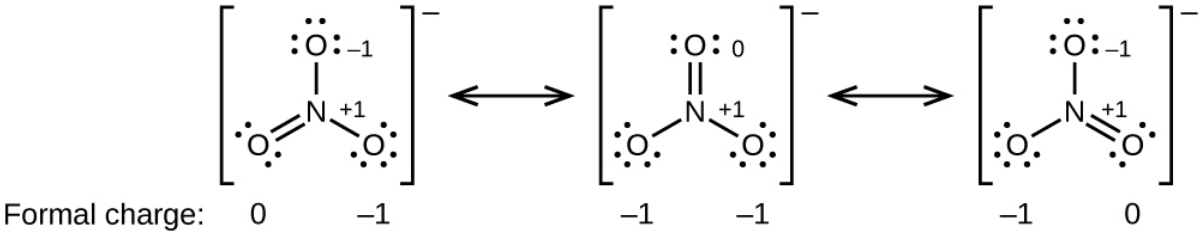
(b)



(c)



(d)

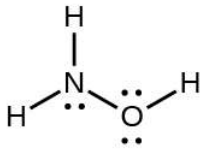


68.

HOCl

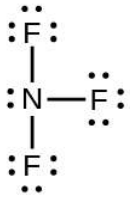
70.

The structure that gives zero formal charges is consistent with the actual structure:

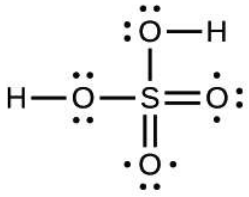


72.

NF_3;



74.



75.

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

77.

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

79.

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

81.

(a) Both the electron geometry and the molecular structure are octahedral. (b) Both the electron geometry and the molecular structure are trigonal bipyramid. (c) Both the electron geometry and the molecular structure are linear. (d) Both the electron geometry and the molecular structure are trigonal planar.

83.

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

85.

(a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

87.

All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, and PH_2^- have dipole moments.

89.

SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

91.

P

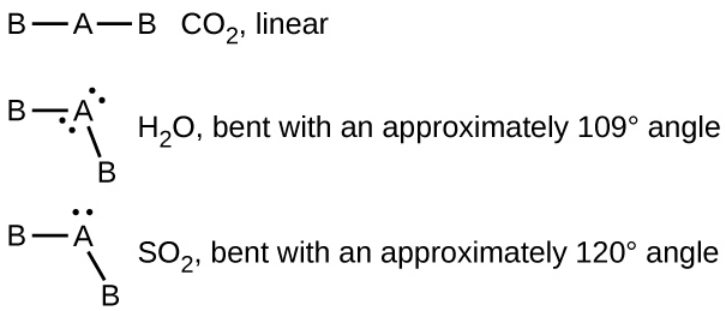
93.

nonpolar

95.

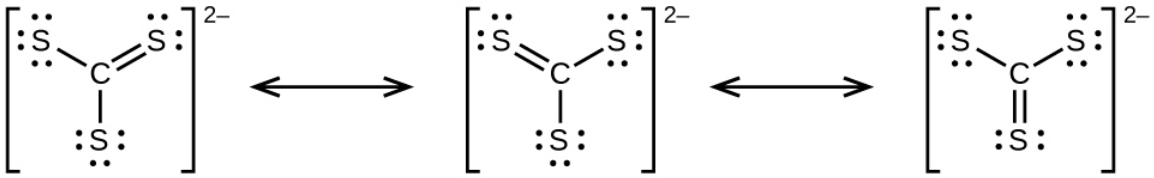
(a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) $\underline{C}H_3CCH$ tetrahedral, $CH_3\underline{C}\underline{C}H$ linear; (h) tetrahedral; (i) $H_2C\underline{C}CH_2$ linear; $H_2\underline{C}\underline{C}\underline{C}H_2$ trigonal planar

97.

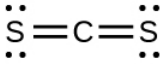


99.

(a)



(b)



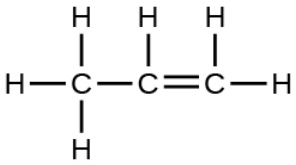
(c)



(d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

101.

The Lewis structure is made from three units, but the atoms must be rearranged:



103.

The molecular dipole points away from the hydrogen atoms.

105.

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

This page titled 4.5.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

4.6: Exercises (Intermolecular Forces)

1.

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

2.

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

3.

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

4.

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

5.

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

6.

Open the PhET States of Matter Simulation to answer the following questions:

(a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?

(b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.

(c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

7.

Define the following and give an example of each:

(a) dispersion force

(b) dipole-dipole attraction

(c) hydrogen bond

8.

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

9.

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

10

10.
Neon and HF have approximately the same molecular masses.

(a) Explain why the boiling points of Neon and HF differ.

(b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

11.

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

(a) HCl, H_2O, SiH_4

(b) F_2, Cl_2, Br_2

(c) CH_4, C_2H_6, C_3H_8

(d) O_2, NO, N_2

12.

The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

13.

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.

14.

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

15.

The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

16.

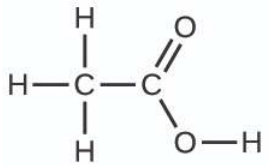
Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

17.

Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

18.

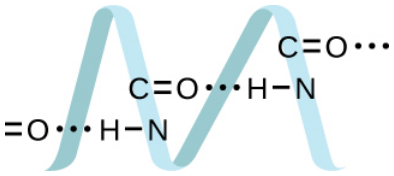
Under certain conditions, molecules of acetic acid, CH_3COOH, form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

19.

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



20.

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

21.

Identify the intermolecular forces present in the following solids:

(a) CH_3CH_2OH

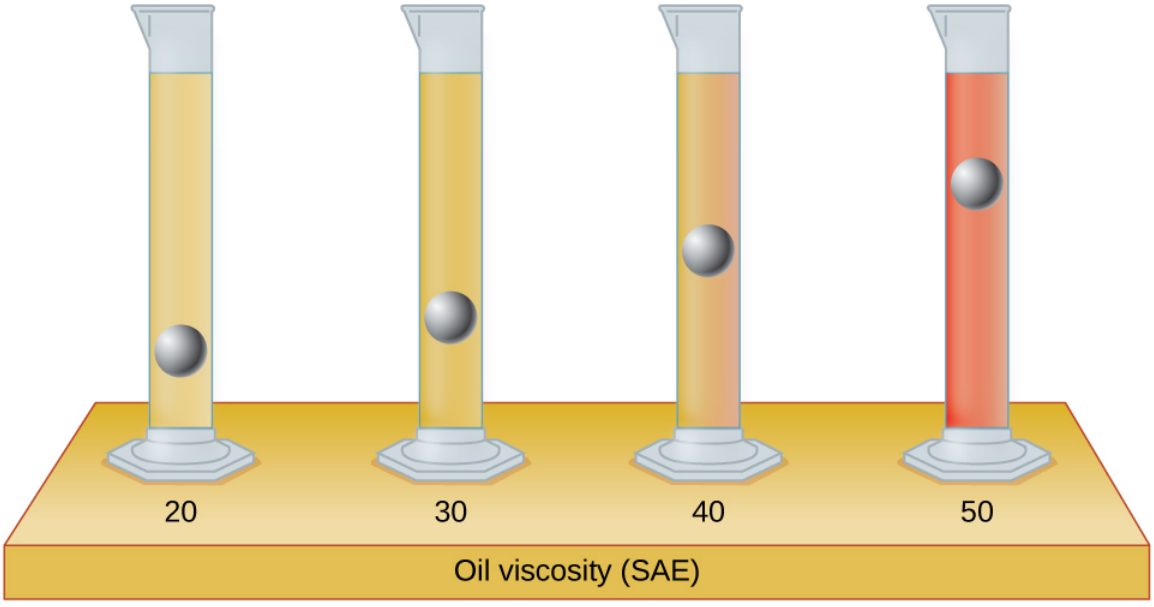
(b) $CH_3CH_2CH_3$

(c) CH_3CH_2Cl

22.

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.

Rank the motor oils in order of increasing viscosity, and explain your reasoning:



23.

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible.

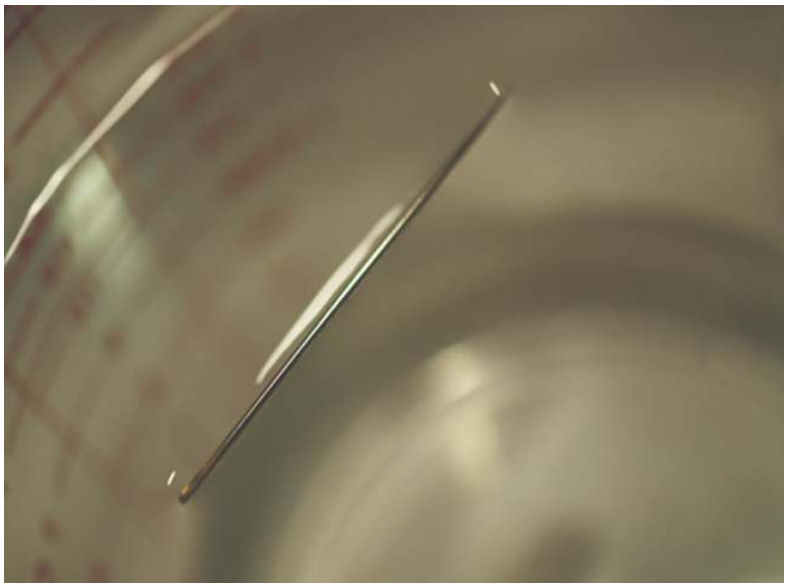
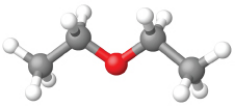
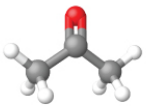
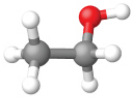
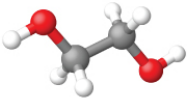


Figure 10.67 (credit: Cory Zanker)

24.

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

(a) Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.

(b) Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

25.

You may have heard someone use the figure of speech “slower than molasses in winter” to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

26.

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

27.

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

28.

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example 10.4 for the required information.

29.

Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

30.

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

31.

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

32.

What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

33.

Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

34.

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

35.

What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

36.

What is the relationship between the intermolecular forces in a solid and its melting temperature?

37.

Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

38.

Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.

39.

When is the boiling point of a liquid equal to its normal boiling point?

40.

How does the boiling of a liquid differ from its evaporation?

41.

Use the information in Figure 10.24 to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

42.

A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

43.

Explain the following observations:

(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).

(b) Perspiring is a mechanism for cooling the body.

44.

The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

45.

Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though the type of IMF (dispersion) is the same.

46.

Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

47.

The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers.

48.

The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

49.

Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

50.

Which contains the compounds listed correctly in order of increasing boiling points?

(a) $N_2 < CS_2 < H_2O < KCl$

(b) $H_2O < N_2 < CS_2 < KCl$

(c) $N_2 < KCl < CS_2 < H_2O$

(d) $CS_2 < N_2 < KCl < H_2O$

(e) $KCl < H_2O < CS_2 < N_2$

51.

How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

52.

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

53.

Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a $\Delta H_{\text{fusion}} = 9.37$ kJ/mol.

(a) How much energy is required to melt 263.1 g $TiCl_4$?

(b) For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{\text{vaporization}}$? Explain your reasoning.

54.

From the phase diagram for water (Figure 10.31), determine the state of water at:

(a) 35 °C and 85 kPa

(b) −15 °C and 40 kPa

(c) −15 °C and 0.1 kPa

(d) 75 °C and 3 kPa

(e) 40 °C and 0.1 kPa

(f) 60 °C and 50 kPa

55.

What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C?

56.

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

57.

From the phase diagram for carbon dioxide in Figure 10.34, determine the state of CO_2 at:

(a) 20 °C and 1000 kPa

(b) 10 °C and 2000 kPa

(c) 10 °C and 100 kPa

(d) −40 °C and 500 kPa

(e) −80 °C and 1500 kPa

(f) −80 °C and 10 kPa

58.

Determine the phase changes that carbon dioxide undergoes as pressure is increased at a constant temperature of (a) −50 °C and (b) 50 °C. If the temperature is held at −40 °C? At 20 °C? (See the phase diagram in Figure 10.34.)

59.

Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

60.

Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure 10.34 for the phase diagram.)

61.

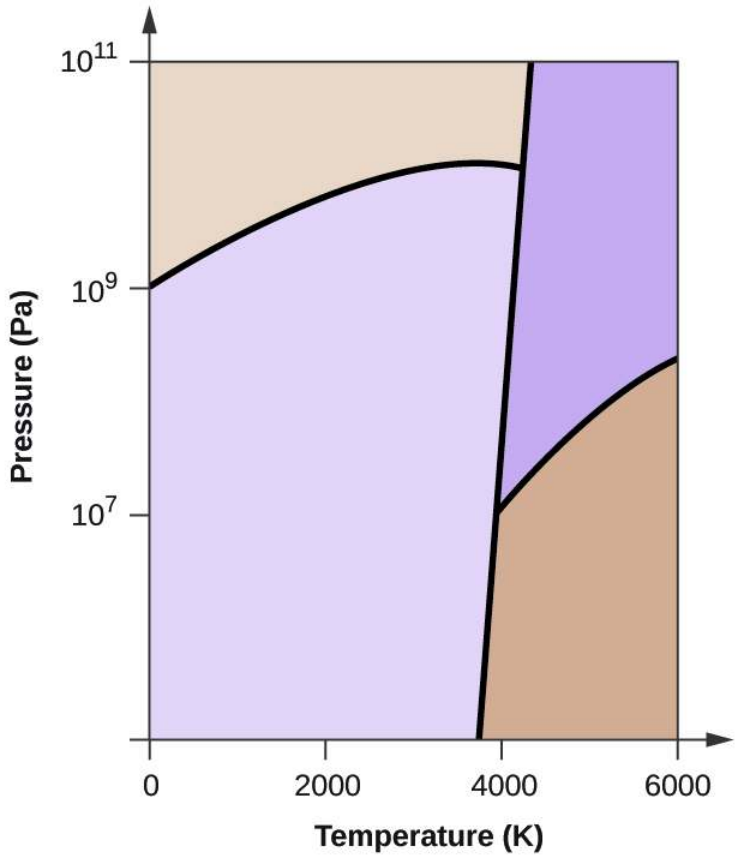
If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

62.

Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

63.

Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram:



(a) On the phase diagram, label the gas and liquid regions.

(b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.

(c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.

(d) Circle each triple point on the phase diagram.

(e) In what phase does carbon exist at 5000 K and 10^{8} Pa?

(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^{6} Pa, which phase transition occurs, if any?

64.

What types of liquids typically form amorphous solids?

65.

At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

(a) ionic

(b) covalent network

(c) metallic

(d) amorphous

(e) molecular crystals

66.

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

(a) ionic

(b) covalent network

(c) metallic

(d) amorphous

(e) molecular crystals

67.

Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

68.

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) SiO_2

(b) KCl

(c) Cu

(d) CO_2

(e) C (diamond)

(f) $BaSO_4$

(g) NH_3

(h) NH_4F

(i) C_2H_5OH

69.

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) $CaCl_2$

(b) SiC

(c) N_2

(d) Fe

(e) C (graphite)

(f) $CH_3CH_2CH_2CH_3$

(g) HCl

(h) NH_4NO_3

(i) K_3PO_4

70.

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

71.

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

72.

Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

73.

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

(a) ionic solid

(b) metallic solid

(c) molecular solid

(d) covalent network solid

74.

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

(a) ionic solid

(b) metallic solid

(c) molecular solid

(d) covalent network solid

75.

Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

76.

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

77.

What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

78.

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

79.

Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

80.

Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

81.

Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

(a) What is the atomic radius of tungsten in this structure?

(b) Calculate the density of tungsten.

82.

Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

83.

Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

(a) What is the atomic radius of barium in this structure?

(b) Calculate the density of barium.

84.

Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

85.

The density of aluminum is 2.7 g/cm^3; that of silicon is 2.3 g/cm^3. Explain why Si has the lower density even though it has heavier atoms.

86.

The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

87.

Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

88.

A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

89.

What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

90.

A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

91.

A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

92.

Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

93.

What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

94.

Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

95.

As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

96.

Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

97.

One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

98.

NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

(a) Calculate the ionic radius of H^-. (The ionic radius of Li^+ is 0.0.95 Å.)

(b) Calculate the density of NaH.

99.

Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of TI^+. (The ionic radius of I^- is 2.16 Å.)

100.

A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

(a) What is the empirical formula of this compound? Explain your answer.

(b) What is the coordination number of the Mn^{3+} ion?

(c) Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 A.

(d) Calculate the density of the compound.

101.

What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

102.

A diffractometer using X-rays with a wavelength of 0.2287 nm produced first order diffraction peak for a crystal angle θ = 16.21°. Determine the spacing between the diffracting planes in this crystal.

103.

A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

104.

Gold crystallizes in a face-centered cubic unit cell. The second-order reflection (n = 2) of X-rays for the planes that make up the tops and bottoms of the unit cells is at θ = 22.20°. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

105.

When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first order diffraction?

This page titled 4.6: Exercises (Intermolecular Forces) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

4.6.1: Answers to Selected Exercises

1.

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

3.

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

5.

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

7.

(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (e.g., Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (e.g., ICI molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (e.g., $\mathbf{HF\cdots HF}$).

9.

The London forces typically increase as the number of electrons increase.

11.

(a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$

13.

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction, therefore, is stronger, leading to a higher boiling point.

15.

−85 °C. Water has stronger hydrogen bonds, so it melts at a higher temperature.

17.

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

19.

H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the $\mathbf{N-H}$ and $\mathbf{C=O}$.

21.

(a) hydrogen bonding, dipole-dipole attraction, and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

23.

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or paper clip if gently placed on the water.

25.

Temperature has an effect on intermolecular forces: The higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid. The lower the temperature, the less the intermolecular forces are overcome, and so the less viscous the liquid.

27.

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

29.

1.7×10^{-4} m

31.

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

33.

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

35.

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

37.

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

39.

They are equal when the pressure of gas above the liquid is exactly 1 atm.

41.

approximately 95 °C

43.

(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

45.

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

47.

The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of −8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

49.

The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

51.

1125 kJ

53.

(a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

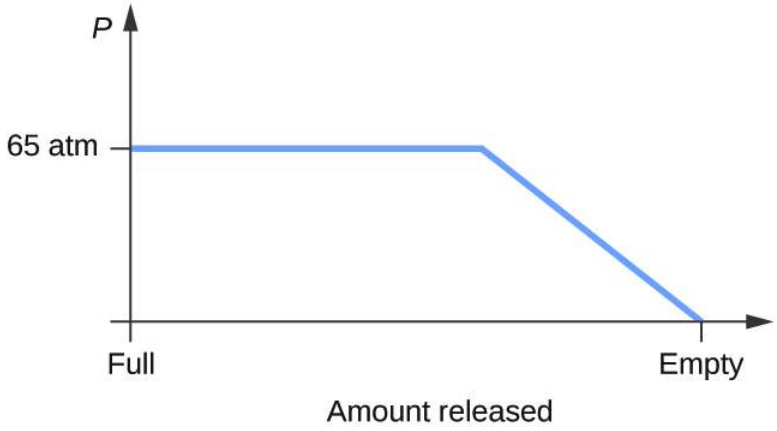
55.

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At −40 °C, water goes from a gas to a solid as the pressure increases above very low values.

57.

(a) gas; (b) gas; (c) gas; (d) gas; (e) solid; (f) gas

59.

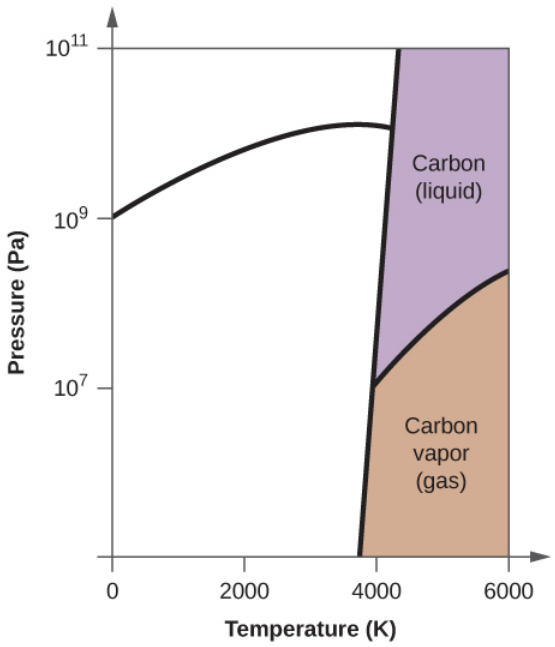


61.

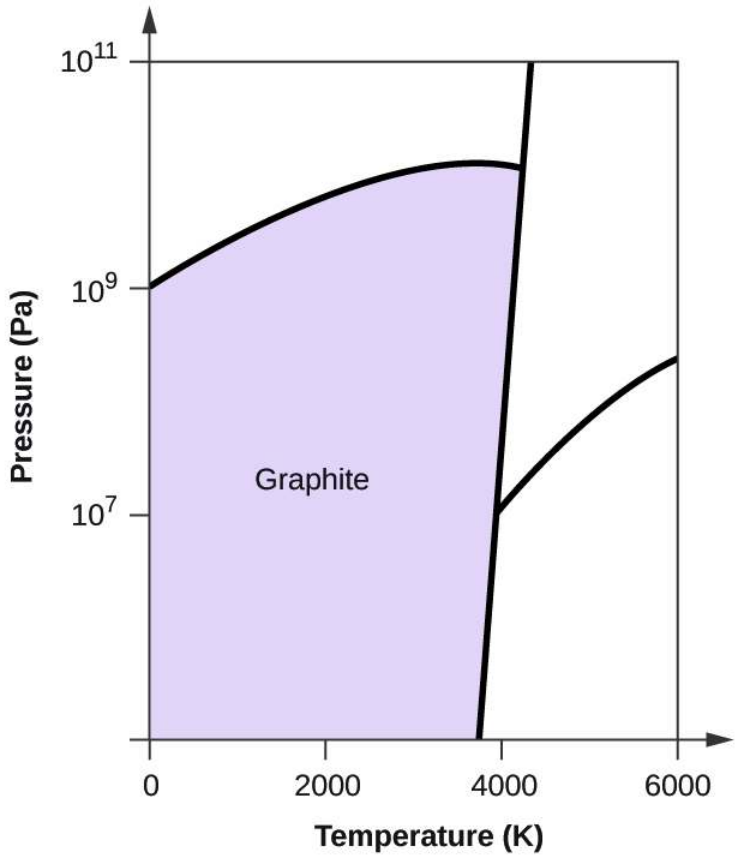
Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

63.

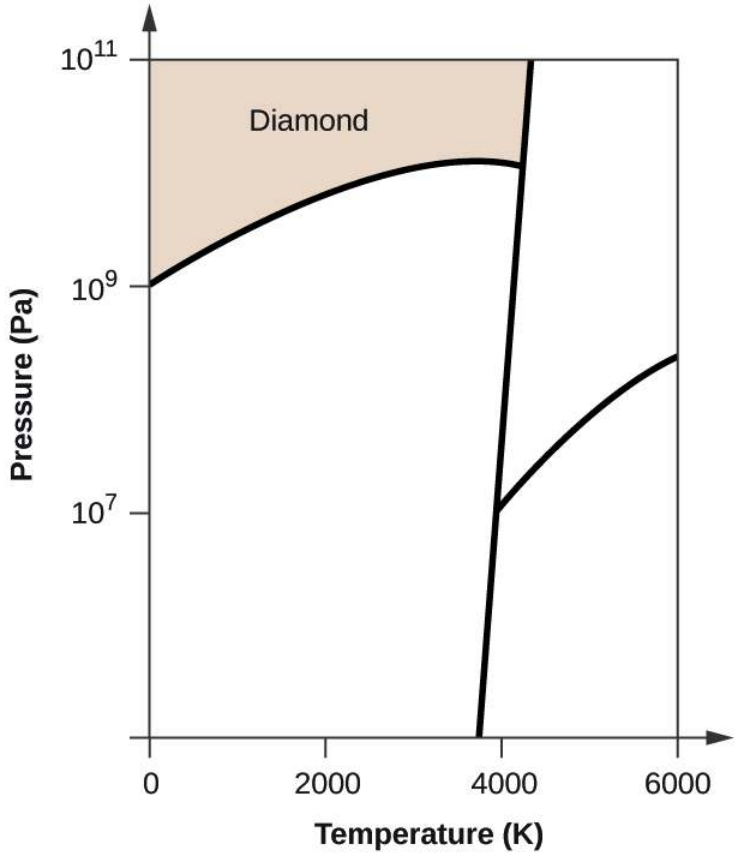
(a)


10^{11}
10^{9}
10^{7}
Pressure (Pa)
Carbon
(liquid)
Carbon
vapor
(gas)
0
2000
4000
6000
Temperature (K)

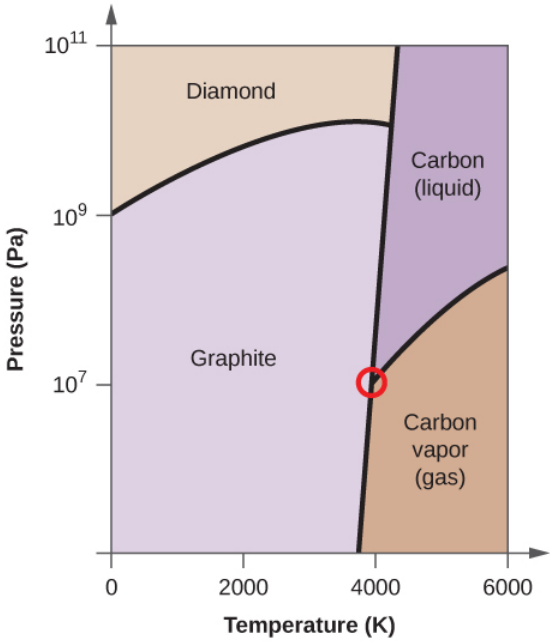
(b)


10^{11}
10^{9}
10^{7}
Pressure (Pa)
Graphite
0
2000
4000
6000
Temperature (K)

(c)



(d)



(e) liquid phase (f) sublimation

65.

(e) molecular crystals

67.

Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

69.

(a) ionic; (b) covalent network; (c) molecular; (d) metallic; (e) covalent network; (f) molecular; (g) molecular; (h) ionic; (i) ionic

71.

X = ionic; Y = metallic; Z = covalent network

73.

(b) metallic solid

75.

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

77.

eight

79.

12

81.

(a) 1.370 Å; (b) 19.26 g/cm

83.

(a) 2.176 Å; (b) 3.595 g/cm^3

85.

The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

87.

In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

89.

Co_3O_4

91.

In a simple cubic array, only one cubic hole can be occupied be a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

93.

59.95%; The oxidation number of titanium is +4.

95.

Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+}.

97.

Mn_2O_3

99.

1.48 Å

101.

2.874 Å

103.

20.2°

105.

1.74×10^4 eV

This page titled 4.6.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

5: Moles, Molar Mass, Concentration, and Solutions

5.1: Formula Mass and the Mole Concept
5.2: Determining Empirical and Molecular Formulas
5.3: Molarity
5.4: The Dissolution Process
5.5: Electrolytes
5.6: Exercises (Solutions and Concentrations)
5.6.1: Answers to Selected Exercises
5.7: Exercises (Moles and Chemical Formulas)
5.7.1: Answers to Selected Exercises (Moles and Chemical Formulas)

This page titled 5: Moles, Molar Mass, Concentration, and Solutions is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

5.1: Formula Mass and the Mole Concept

Learning Objectives

By the end of this section, you will be able to:

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro's number Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another

Many argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

5.1.1: Formula Mass

An earlier chapter of this text described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the formula mass of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

5.1.1.1: Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 5.1.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

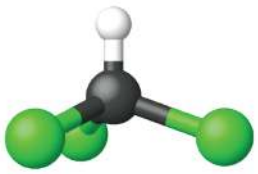


Figure 5.1.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure 5.1.2).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

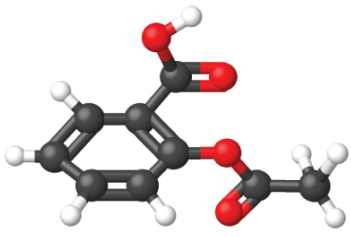


Figure 5.1.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

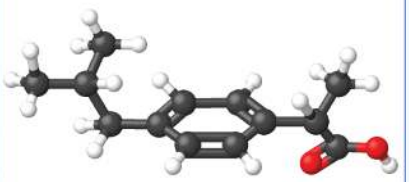
Example 5.1.1: Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are composed of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.144
O	2	×	16.00	=	32.00
				Molecular mass	206.27



Exercise 5.1.1

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Answer

151.16 amu

5.1.1.2: Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see Figure **5.1.3**).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

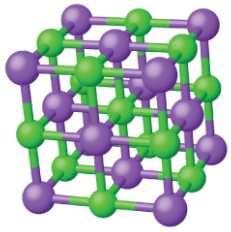


Figure **5.1.3**: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

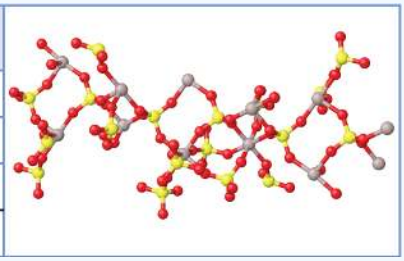
Example 5.1.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



Exercise 5.1.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Answer

310.18 amu

5.1.2: The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, sophisticated instruments allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The *mole* is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a sample of matter. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth. A mole of substance is that amount in which there are $6.02214076 \times 10^{23}$.

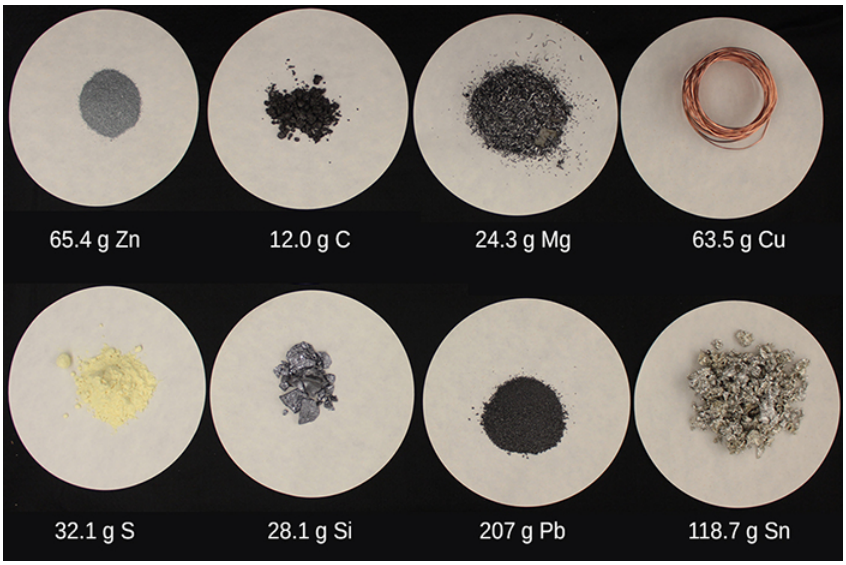


Figure **5.1.4**: Each sample contains 6.022 10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

The molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). A mole of ^{12}C weighs 12 g (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure **5.1.5**).



Figure **5.1.5**: Each sample contains 6.02 10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022 10^{23}
H	1.008	1.008	6.022 10^{23}
O	16.00	16.00	6.022 10^{23}
Na	22.99	22.99	6.022 10^{23}
Cl	35.45	35.45	6.022 10^{23}

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see Figure **5.1.6**). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



Figure **5.1.6**: The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: "tanakawho"/Wikimedia commons)

Link to Learning

The mole is used in chemistry to represent 6.022 10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds, as demonstrated in the next several example problems.

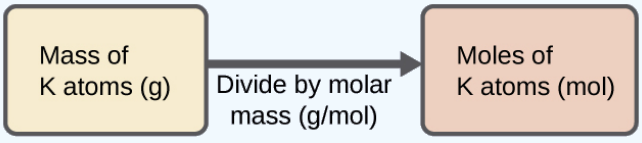
Example 5.1.3: Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

$$4.7\ \cancel{\text{g K}}\left(\frac{\text{mol K}}{39.10\ \cancel{\text{g K}}}\right) = 0.12\,\text{mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol,

Exercise 5.1.3

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Answer

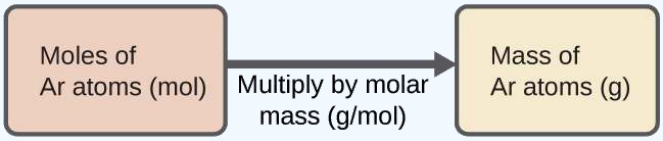
0.360 mol

Example 5.1.4: Deriving Grams from Moles for an Element

A liter of air contains 9.2 10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth (~10^{-3}) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4} \cancel{\text{mol Ar}} \left(\frac{39.95\ \text{g Ar}}{\cancel{\text{mol Ar}}} \right) = 0.037\ \text{g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 5.1.1

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 5.1.5: Deriving Number of Atoms from Mass for an Element

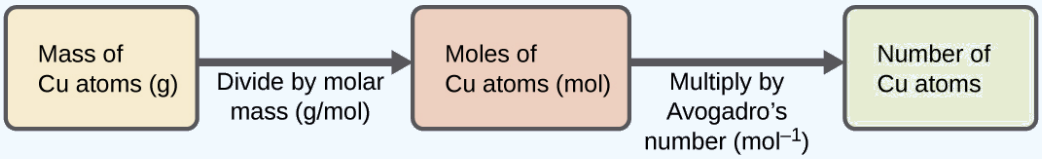
Copper is commonly used to fabricate electrical wire (Figure 5.1.7). How many copper atoms are in 5.00 g of copper wire?



Figure 5.1.7: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00\ \cancel{\text{g Cu}}\left(\frac{\cancel{\text{mol Cu}}}{63.55\ \cancel{\text{g Cu}}}\right)\left(\frac{6.022\times10^{23}\text{Cu atoms}}{\cancel{\text{mol Cu}}}\right)=4.74\times10^{22}\ \text{Cu atoms}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

? Exercise 5.1.5

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Answer

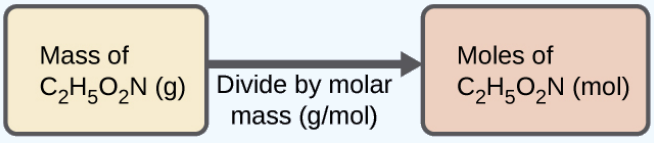
4.586×10^{22} Au atoms

✓ Example 5.1.6: Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

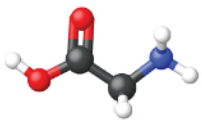
Solution

Derive the number of moles of a compound from its mass following the same procedure used for an element in Example 5.1.3:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so the computed result is expected to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

$$28.35 \cancel{\text{ g glycine}} \left(\frac{\text{mol glycine}}{75.07 \cancel{\text{ g glycine}}} \right) = 0.378 \text{ mol glycine}$$

This result is consistent with the rough estimate,

? Exercise 5.1.6

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

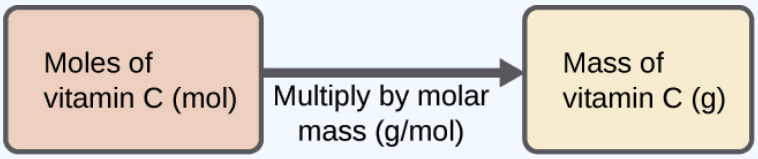
0.073 mol

✓ Example 5.1.7: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is $1.42\ 10^{-4}$ mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, the corresponding mass is expected to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation yields:

$$1.42 \times 10^{-4} \cancel{\text{ mol vitamin C}} \left(\frac{176.124 \text{ g vitamin C}}{\cancel{\text{mol vitamin C}}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

? Exercise 5.1.7

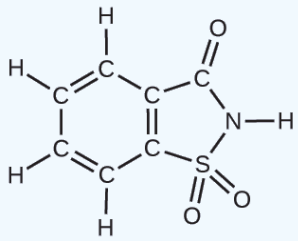
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

14.2 g

Example 5.1.8: Deriving the Number of Atoms and Molecules from the Mass of a Compound

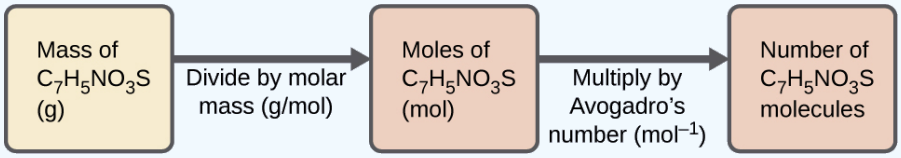
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Example **5.1.6**, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \cancel{\text{g } C_7H_5NO_3S}\left(\frac{\cancel{\text{mol } C_7H_5NO_3S}}{183.18\ \cancel{\text{g } CH_5NO_3S}}\right)\left(\frac{6.022\times10^{23}\ {}_7CH_5NO_3S\text{ molecules}}{1\ \cancel{\text{mol } C_7H_5NO_3S}}\right)$$
$$= 1.31\times10^{20}\ {}_7CH_5NO_3S\text{ molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31\times10^{20}\ {}_7CH_5NO_3S\text{ molecules}\left(\frac{7\text{ C atoms}}{1\ {}_7CH_5NO_3S\text{ molecule}}\right) = 9.17\times10^{20}\text{ C atoms}$$

Exercise 5.1.8

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Answer

9.545×10^{22} molecules C_4H_{10}

9.545×10^{23} atoms H

How Sciences Interconnect: Counting Neurotransmitter Molecules in the Brain

The brain is the control center of the central nervous system (Figure **5.1.8**). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these

advances through the concerted efforts of various industrial, academic, and government agencies (more details available at www.whitehouse.gov/share/brain-initiative).

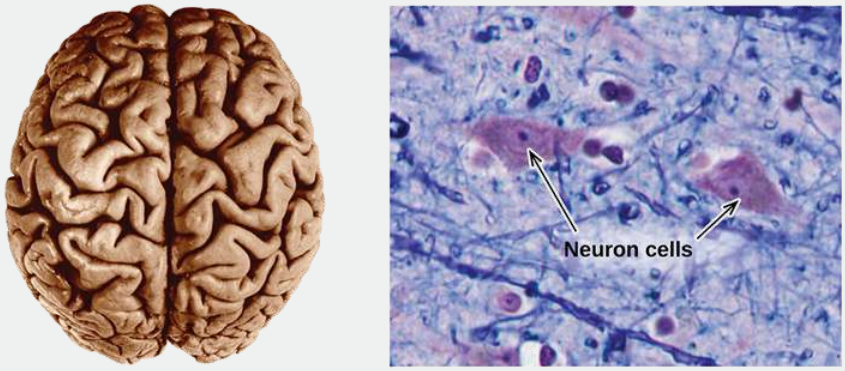


Figure **5.1.8**: (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse) and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell membrane and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see Figure **5.1.9**). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.

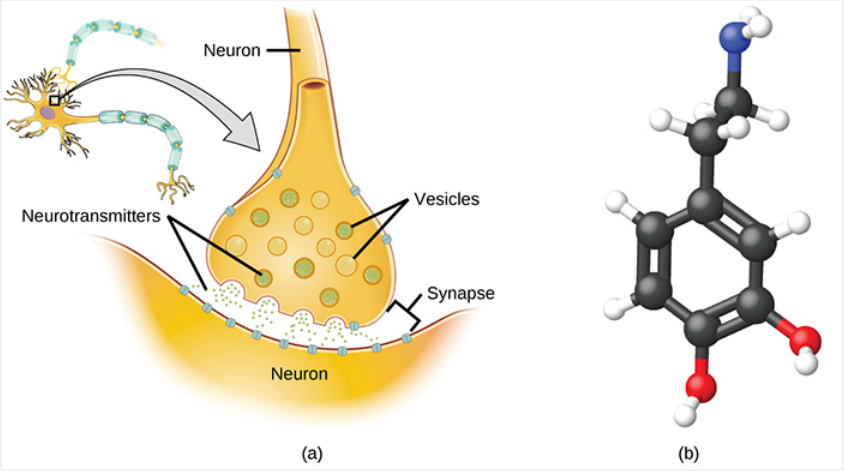


Figure **5.1.9**: (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can

selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle (about 5×10^{-20} mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.

5.1.3: Footnotes

- 1Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

This page titled 5.1: Formula Mass and the Mole Concept is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **3.1: Formula Mass and the Mole Concept** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.2: Determining Empirical and Molecular Formulas

Learning Objectives

By the end of this section, you will be able to:

- Compute the percent composition of a compound
- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

The previous section discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, one may determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, these same principles will be applied to derive the chemical formulas of unknown substances from experimental mass measurements.

5.2.1: Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's **percent composition**, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%H = \frac{\text{mass } H}{\text{mass compound}} \times 100\%$$
$$\%C = \frac{\text{mass } C}{\text{mass compound}} \times 100\%$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%H = \frac{2.5gH}{10.0g \text{ compound}} \times 100\% = 25\%$$
$$\%C = \frac{7.5gC}{10.0g \text{ compound}} \times 100\% = 75\%$$

Example 5.2.1: Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%C = \frac{7.34gC}{12.04g \text{ compound}} \times 100\% = 61.0\%$$
$$\%H = \frac{1.85gH}{12.04g \text{ compound}} \times 100\% = 15.4\%$$
$$\%N = \frac{2.85gN}{12.04g \text{ compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

? Exercise 5.2.1

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Answer

12.1% C, 16.1% O, 71.79% Cl

5.2.1.1: Determining Percent Composition from Molecular or Empirical Formulas

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%N = \frac{14.01 amu N}{17.03 amu HH} \times 100\% = 82.27\%$$
$$\%H = \frac{3.024 amu H}{17.03 amu H} \times 100\% = 17.76\%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example **5.2.2**. As long as the molecular or empirical formula of the compound in question is known, the percent composition may be derived from the atomic or molar masses of the compound's elements.

✓ Example 5.2.2: Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

Solution

To calculate the percent composition, the masses of C, H, and O in a known mass of $C_9H_8O_4$ are needed. It is convenient to consider 1 mol of $C_9H_8O_4$ and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\%C = \frac{9 mol C \times \text{ molar mass } C}{\text{molar mass } C_9H_8O_4} \times 100 = \frac{9 \times 12.01 g/mol}{180.159 g/mol} \times 100 = \frac{108.09 g/mol}{180.159 g/mol} \times 100$$
$$\%C = 60.00\%C$$

$$\%H = \frac{8 mol H \times \text{ molar mass } H}{\text{molar mass } C_9H_8O_4} \times 100 = \frac{8 \times 1.008 g/mol}{180.159 g/mol} \times 100 = \frac{8.064 g/mol}{180.159 g/mol} \times 100$$
$$\%H = 4.476\%H$$

$$\%O = \frac{4 mol O \times \text{ molar mass}}{\text{molar mass } C_9H_8O_4} \times 100 = \frac{4 \times 16.00 g/mol}{180.159 g/mol} \times 100 = \frac{64.00 g/mol}{180.159 g/mol} \times 100$$
$$\%O = 35.52\%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

? Exercise 5.2.2

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3?

Answer

69.9% Fe

5.2.2: Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. This is accomplished using molar masses to convert the mass of each element to a number of moles. These molar amounts are used to compute whole-number ratios that can be used to derive the empirical formula of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.71 gC \times \frac{1 molC}{12.01 gC} = 0.142 molC$$
$$0.287 gH \times \frac{1 molH}{1.008 gH} = 0.284 molH$$

Thus, this compound may be represented by the formula $C_{0.142}H_{0.284}$. Per convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$C_{\frac{0.142}{0.142}} H_{\frac{0.284}{0.142}} \text{ or } CH_2$$

(Recall that subscripts of "1" are not written but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or may not be the compound's *molecular formula* as well; however, additional information is needed to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$Cl_{0.150}O_{0.525} = Cl_{\frac{0.150}{0.150}} O_{\frac{0.525}{0.150}} = ClO_{3.5}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure **5.2.1** outlines this procedure in flow chart fashion for a substance containing elements A and X.

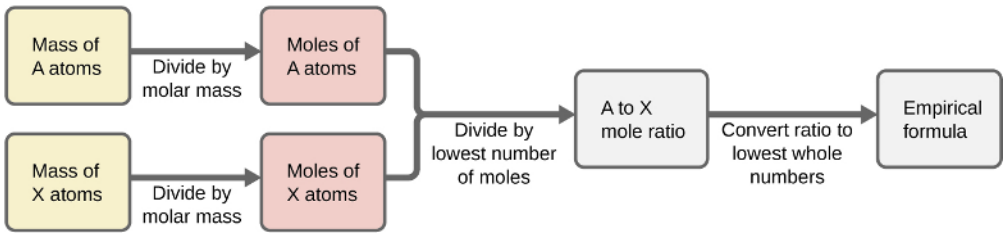


Figure **5.2.1**: The empirical formula of a compound can be derived from the masses of all elements in the sample.

Example **5.2.3**: Determining a Compound's Empirical Formula from the Masses of Its Elements

A sample of the black mineral hematite (Figure **5.2.2**), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



Figure 5.2.2: Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

This problem provides the mass in grams of each element. Begin by finding the moles of each:

$$34.97 g Fe \left(\frac{mol Fe}{55.85 g} \right) = 0.6261 mol Fe$$
$$15.03 g O \left(\frac{mol O}{16.00 g} \right) = 0.9394 mol O$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000 mol Fe$$
$$\frac{0.9394}{0.6261} = 1.500 mol O$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2 \left(Fe_1O_{1.5} \right) = Fe_2O_3$$

The empirical formula is Fe_2O_3.

Exercise 5.2.3

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer

N_2O_5

Link to Learning

For additional worked examples illustrating the derivation of empirical formulas, watch the brief video clip.

5.2.2.1: Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

Example 5.2.4: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure 5.2.3). What is the empirical formula for this gas?



Figure **5.2.3**: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the "percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\%C = \frac{27.29gC}{100g \text{ compound}}$$
$$72.71\%O = \frac{72.71gO}{100g \text{ compound}}$$

The molar amounts of carbon and oxygen in a 100-g sample are calculated by dividing each element's mass by its molar mass:

$$27.29gC\left(\frac{molC}{12.01g}\right) = 2.272molC$$
$$72.71gO\left(\frac{molo}{16.00g}\right) = 4.544molO$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272molC}{2.272} = 1$$
$$\frac{4.544molO}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

? Exercise 5.2.4

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Answer

CH_2O

5.2.3: Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its

molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its **empirical formula mass**. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If the molecular (or molar) mass of the substance is known, it may be divided by the empirical formula mass to yield the number of empirical formula units per molecule (n):

$$\frac{\text{molecular or molar mass (amu or } \frac{\text{g}}{\text{mol}})}{\text{empirical formula mass (amu or } \frac{\text{g}}{\text{mol}})} = n \text{ formula units/molecule}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by n, as shown by the generic empirical formula A_xB_y:

$$(A_xB_y)_n = A_{nx}B_{ny}$$

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180 \text{ amu / molecule}}{30 \frac{\text{amu}}{\text{formula unit}}} = 6 \text{ formula units / molecule}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, *one mole* of empirical formula units and molecules is considered, as opposed to single units and molecules.

Example 5.2.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02gC)\left(\frac{1molC}{12.01gC}\right) = 6.163molC$$
$$(8.710gH)\left(\frac{1molH}{1.008gH}\right) = 8.641molH$$
$$(17.27gN)\left(\frac{1molN}{14.01gN}\right) = 1.233molN$$

Next, calculate the molar ratios of these elements relative to the least abundant element, N.

$$6.163 \text{ mol C}/1.233 \text{ mol N} = 58.641 \text{ mol H}/1.233 \text{ mol N} = 71.233 \text{ mol N}/1.233 \text{ mol N} = 1$$

$$\frac{1.233}{1.233} = 1.000 mol N$$
$$\frac{6.163}{1.233} = 4.998 mol C$$
$$\frac{8.624}{1.233} = 6.994 mol H$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

Calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57 g \text{ nicotine}}{0.2500 mol \text{ nicotine}} = \frac{162.3 g}{mol}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3 g/mol}{81.13 \frac{g}{\text{formula unit}}} = 2 \text{ formula units / molecule}$$

Finally, derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

? Exercise 5.2.1

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer

$C_8H_{10}N_4O_2$

This page titled 5.2: Determining Empirical and Molecular Formulas is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **3.2: Determining Empirical and Molecular Formulas** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.3: Molarity

Learning Objectives

By the end of this section, you will be able to:

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

Preceding sections of this chapter focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see Figure **5.3.1**). This section will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Figure **5.3.1**: Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

5.3.1: Solutions

Solutions have previously been defined as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. A more thorough treatment of solution properties is provided in the chapter on solutions and colloids, but provided here is an introduction to some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the solvent and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity** (*M*) is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Example 5.3.1: Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133\,\text{mol}}{355\,\text{mL} \times \frac{1\,\text{L}}{1000\,\text{mL}}} = 0.375M$$

Exercise 5.3.1

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer

0.05 *M*

Example 5.3.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example **5.3.1**?

Solution

Rearrange the definition of molarity to isolate the quantity sought, moles of sugar, then substitute the value for molarity derived in Example **5.3.1**, 0.375 *M*:

$$\begin{aligned} M &= \frac{\text{mol solute}}{L\text{ solution}} \\ \text{mol solute} &= M \times L\text{ solution} \\ &= 0.375\frac{\text{mol sugar}}{L} \times \left(10\,\text{mL} \times \frac{1\,\text{L}}{1000\,\text{mL}}\right) \\ &= 0.004\,\text{mol sugar} \end{aligned}$$

Exercise 5.3.2

What volume (mL) of the sweetened tea described in Example **5.3.1** contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

Example 5.3.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure **5.3.2**) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Figure 5.3.2: Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. Since the mass of solute is provided instead of its molar amount, use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\,\text{g}\,CH_3CO_2H \times \frac{1\,\text{mol}\,CH_3CO_2H}{60.052\,\text{g}\,CH_3CO_2H}}{0.500\,\text{L solution}} = 0.839\,\text{M}$$

Exercise 5.3.3

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 *M*

Example 5.3.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 5.3.2:

$$\begin{aligned} M &= \frac{\text{mol solute}}{L\text{ solution}} \\ \text{mol solute} &= M \times L\text{ solution} \\ &= 5.30\frac{\text{mol NaCl}}{\text{L}} \times 0.250L \\ &= 1.325\,\text{mol NaCl} \end{aligned}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\,\text{mol NaCl} \times \frac{58.44\,\text{g NaCl}}{1\,\text{mol NaCl}} = 77.4\,\text{g NaCl}$$

Exercise 5.3.4

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-*M* solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in Example **5.3.4**, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example **5.3.4**, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If the guard digit had not been retained, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, rounding errors may also be avoided by performing computations in a single step (see Example **5.3.5**). This eliminates intermediate steps so that only the final result is rounded.

✔ Example 5.3.5: Determining the Volume of Solution Containing a Given Mass of Solute

In Example **5.3.3**, the concentration of acetic acid in white vinegar was determined to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

$$\text{g solute} \times \left(\frac{\text{mol solute}}{\text{g solute}}\right) \times \left(\frac{\text{L solution}}{\text{mol solute}}\right) = \text{L solution}$$

$$75.6\,\text{g}\,CH_3CO_2H \left(\frac{\text{mol}\,CH_3CO_2H}{60.05\,\text{g}}\right) \left(\frac{\text{L solution}}{0.839\,\text{mol CH 3}\,CO_2H}\right) = 1.50\,\text{L solution}$$

? Exercise 5.3.5

What volume of a 1.50-*M* KBr solution contains 66.0 g **KBr**?

Answer

0.370 L

5.3.2: Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure **5.3.3**).

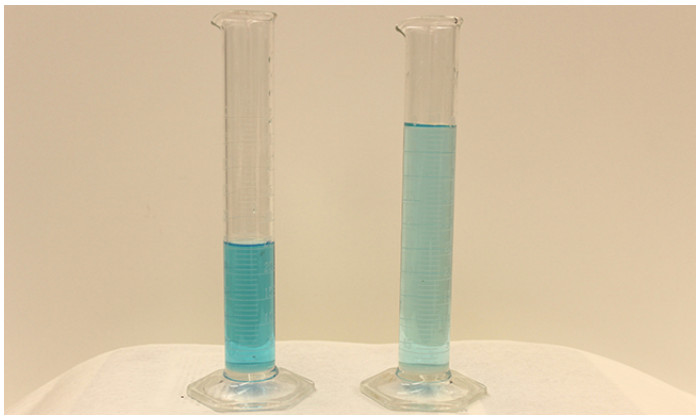


Figure **5.3.3**: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, a solution of lesser concentration may be prepared. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents.

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the number of moles of solute in a solution (n) is equal to the product of the solution's molarity (M) and its volume in liters (L):

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1L_1$$
$$n_2 = M_2L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution*, $n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1L_1 = M_2L_2$$

This relation is commonly referred to as the dilution equation. Although this equation uses molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used as long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1V_1 = C_2V_2$$

where \(C\) and \(V\) are concentration and volume, respectively.

Link to Learning

Use the simulation to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

Example 5.3.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

The stock concentration, C_1, and volume, V_1, are provided as well as the volume of the diluted solution, V_2. Rearrange the dilution equation to isolate the unknown property, the concentration of the diluted solution, C_2:

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), the diluted solution's concentration is expected to be less than one-half 5 *M*. This ballpark estimate will be compared to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850L \times 5.00\frac{mol}{L}}{1.80L} = 2.36M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

? Exercise 5.3.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-*M* solution of CH_3OH to 500.0 mL?

Answer

0.102 *M* CH_3OH

✓ Example 5.3.7: Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

Provided are the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. Find the volume of the diluted solution, V_2 by rearranging the dilution equation to isolate V_2:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), the volume of the diluted solution is expected to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\,\text{M})(0.011\,\text{L})}{(0.12\,\text{M})}$$

$$= 0.041L$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with the rough estimate.

? Exercise 5.3.7

A laboratory experiment calls for 0.125 *M* HNO_3. What volume of 0.125 *M* HNO_3 can be prepared from 0.250 L of 1.88 *M* HNO_3?

Answer

3.76 L

✓ Example 5.3.8: Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

Given are the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. Find the volume of the stock solution, V_1 by rearranging the dilution equation to isolate V_1:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), the volume of the stock solution is expected to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\,\text{M})(5.00\,\text{L})}{1.59\,\text{M}}$$

$$= 0.314\,\text{L}$$

Thus, 0.314 L of the 1.59-*M* solution is needed to prepare the desired solution. This result is consistent with the rough estimate.

? Exercise 5.3.8

What volume of a 0.575-*M* solution of glucose ($\mathbf{C_6H_{12}O_6}$) can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

Answer

0.261 L

This page titled 5.3: Molarity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **3.3: Molarity** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.4: The Dissolution Process

Learning Objectives

By the end of this section, you will be able to:

- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the *solvent*. The other components of the solution present in relatively lesser concentrations are called *solutes*. Sugar is a covalent solid composed of sucrose molecules, $C_{12}H_{22}O_{11}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$C_{12}H_{22}O_{11}\,(s) \longrightarrow C_{12}H_{22}O_{11}\,(aq)$$

The subscript "*aq*" in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to "settle out" over time.

Potassium dichromate, $K_2Cr_2O_7$, is an ionic compound composed of colorless potassium ions, K^+, and orange dichromate ions, $Cr_2O_7^{2-}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 5.4.1), as indicated in this equation:

$$K_2Cr_2O_7\,(s) \longrightarrow 2\,K^+\,(aq) + Cr_2O_7^{2-}\,(aq)$$

As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



Figure 5.4.1: When potassium dichromate ($K_2Cr_2O_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

Link to Learning

Visit this virtual lab to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many alloys are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. Table 5.4.1 gives examples of several different solutions and the phases of the solutes and solvents.

Table 5.4.1: Different Types of Solutions

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks[1]	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in Table **5.4.1**.
- The components of a solution are dispersed on a molecular scale; they consist of a mixture of separated solute particles (molecules, atoms, and/or ions) each closely surrounded by solvent species.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously (within limits determined by the *solubility* of the components, discussed in detail later in this chapter).

5.4.1: The Formation of Solutions

The formation of a solution is an example of a spontaneous process, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes a mixture is stirred to speed up the dissolution process, but this is not necessary; a homogeneous solution will form eventually. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increased dispersal of matter in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in matter dispersal always results when a solution forms from the uniform distribution of solute molecules throughout a solvent.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an ideal solution. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution (Figure **5.4.2**). The formation of this solution clearly involves an increase in matter dispersal, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

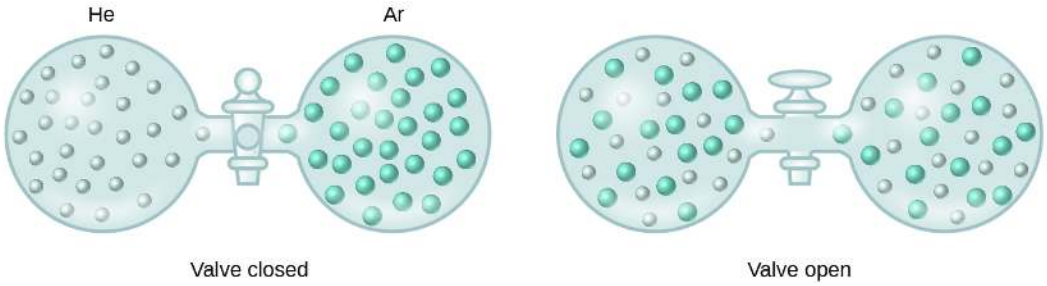


Figure **5.4.2**: Samples of helium and argon spontaneously mix to give a solution.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol (C_2H_5OH) form ideal solutions, as do mixtures of the hydrocarbons pentane, C_5H_{12}, and hexane, C_6H_{14}. Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in Figure **5.4.2**: will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how increased matter dispersal alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure **5.4.3**: , the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as solvation). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.

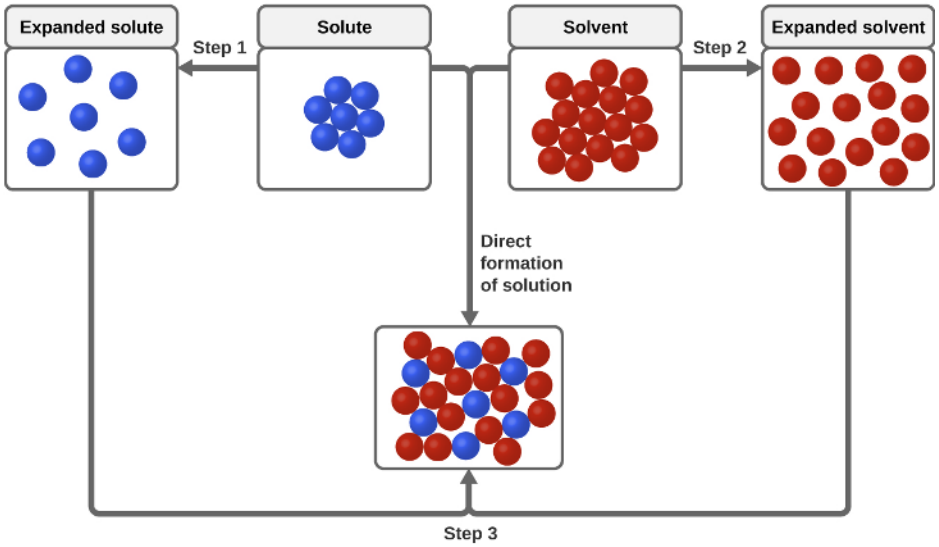


Figure **5.4.3**: This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

Consider the example of an ionic compound dissolving in water. Formation of the solution requires the electrostatic forces between the cations and anions of the compound (solute–solute) be overcome completely as attractive forces are established between these ions and water molecules (solute–solvent). Hydrogen bonding between a relatively small fraction of the water molecules must also be overcome to accommodate any dissolved solute. If the solute's electrostatic forces are significantly greater than the solvation

forces, the dissolution process is significantly endothermic and the compound may not dissolve to an appreciable extent. Calcium carbonate, the major component of coral reefs, is one example of such an “insoluble” ionic compound. On the other hand, if the solvation forces are much stronger than the compound’s electrostatic forces, the dissolution is significantly exothermic and the compound may be highly soluble. common example of this type of ionic compound is sodium hydroxide, commonly known as lye.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs, like the one pictured in Figure **5.4.4**, which are used for treating injuries. A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3. When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.



Figure **5.4.4**: An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

Link to Learning

Watch this brief video illustrating endothermic and exothermic dissolution processes.

5.4.2: Footnotes

- 1If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.

This page titled 5.4: The Dissolution Process is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **11.1: The Dissolution Process** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.5: Electrolytes

Learning Objectives

By the end of this section, you will be able to:

- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called nonelectrolytes. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 5.5.1).

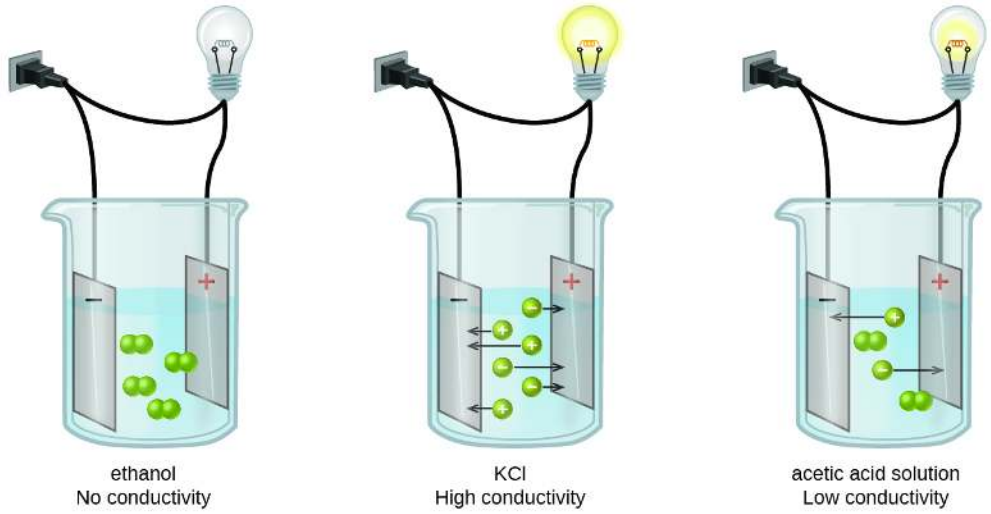


Figure 5.5.1: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

5.5.1: Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 5.5.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

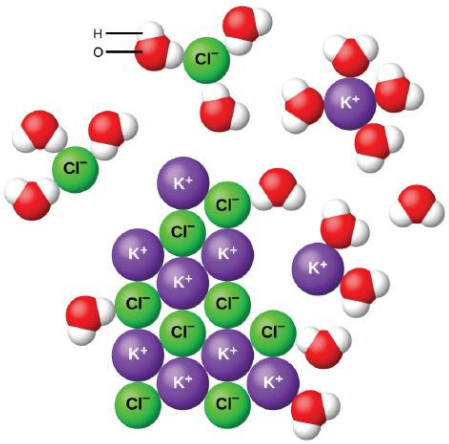


Figure 5.5.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes. Even sparingly, soluble ionic compounds are strong electrolytes, since the small amount that does dissolve will dissociate completely.

Consider what happens at the microscopic level when solid KCl is added to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules surround individual K^+ and Cl^- ions, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure 5.5.2 shows. Overcoming the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution as the ions transition from fixed positions in the undissolved compound to widely dispersed, solvated ions in solution.

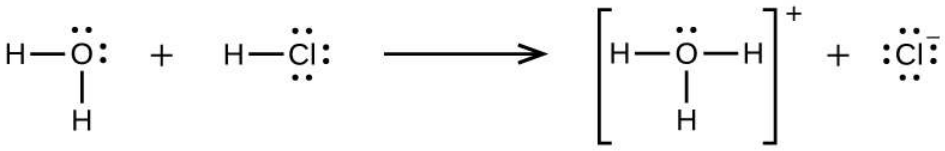
5.5.2: Covalent Electrolytes

Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton (H^+ ion) to another molecule of water, yielding hydronium and hydroxide ions.

$$\mathbf{H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)}$$

In some cases, solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, an aqueous solution of HCl is a very good conductor, indicating that an appreciable concentration of ions exists within the solution.

Because HCl is an *acid*, its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

This page titled 5.5: Electrolytes is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **11.2: Electrolytes** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

5.6: Exercises (Solutions and Concentrations)

1.

What is the total mass (amu) of carbon in each of the following molecules?

(a) CH_4

(b) $CHCl_3$

(c) $C_{12}H_{10}O_6$

(d) $CH_3CH_2CH_2CH_2CH_3$

2.

What is the total mass of hydrogen in each of the molecules?

(a) CH_4

(b) $CHCl_3$

(c) $C_{12}H_{10}O_6$

(d) $CH_3CH_2CH_2CH_2CH_3$

3.

Calculate the molecular or formula mass of each of the following:

(a) P_4

(b) H_2O

(c) $Ca(NO_3)_2$

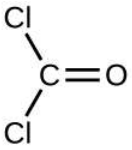
(d) CH_3CO_2H (acetic acid)

(e) $C_{12}H_{22}O_{11}$ (sucrose, cane sugar)

4.

Determine the molecular mass of the following compounds:

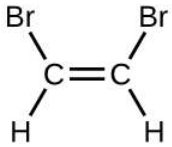
(a)



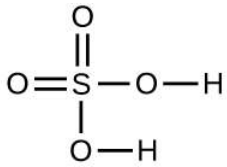
(b)



(c)



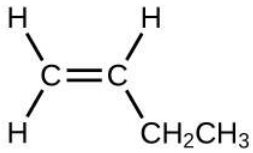
(d)



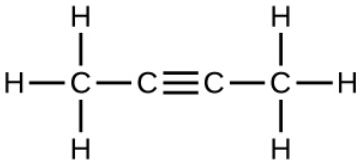
5.

Determine the molecular mass of the following compounds:

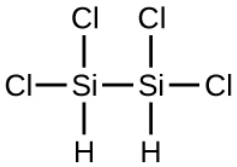
(a)



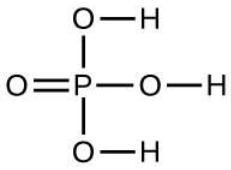
(b)



(c)



(d)



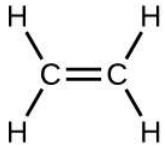
6.

Which molecule has a molecular mass of 28.05 amu?

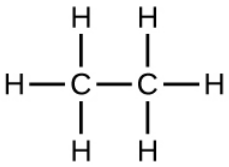
(a)



(b)



(c)



7.

What information is needed to determine the molecular formula of a compound from the empirical formula?

8.

Calculate the following to four significant figures:

(a) the percent composition of ammonia, NH_3

(b) the percent composition of photographic fixer solution "hypo," $Na_2S_2O_3$

(c) the percent of calcium ion in $Ca_3(PO_4)_2$

9.

Determine the following to four significant figures:

(a) the percent composition of hydrazoic acid, HN_3

(b) the percent composition of TNT, $C_6H_2(CH_3)(NO_2)_3$

(c) the percent of SO_4^{2-} in $Al_2(SO_4)_3$

10.

Determine the percent ammonia, NH_3, in $Co(NH_3)_6Cl_3$, to three significant figures.

11.

Determine the percent water in $CuSO_4 \cdot 5H_2O$ to three significant figures.

12.

Determine the empirical formulas for compounds with the following percent compositions:

(a) 15.8% carbon and 84.2% sulfur

(b) 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen

13.

Determine the empirical formulas for compounds with the following percent compositions:

(a) 43.6% phosphorus and 56.4% oxygen

(b) 28.7% K, 1.5% H, 22.8% P, and 47.0% O

14.

A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula?

15.

Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3% carbon and 4.1% hydrogen. What is its molecular formula?

16.

Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol.

17.

Polymers are large molecules composed of simple units repeated many times. Thus, they often have relatively simple empirical formulas. Calculate the empirical formulas of the following polymers:

(a) Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O

(b) Saran; 24.8% C, 2.0% H, 73.1% Cl

(c) polyethylene; 86% C, 14% H

(d) polystyrene; 92.3% C, 7.7% H

(e) Orlon; 67.9% C, 5.70% H, 26.4% N

18.

A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95% C, 17.72% N, and 6.33% H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye.

19.

Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

20.

What information is needed to calculate the molarity of a sulfuric acid solution?

21.

A 200-mL sample and a 400-mL sample of a solution of salt have the same molarity. In what ways are the two samples identical? In what ways are these two samples different?

22.

Determine the molarity for each of the following solutions:

(a) 0.444 mol of $CoCl_2$ in 0.654 L of solution

(b) 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution

(c) 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution

(d) 10.5 kg of $Na_2SO_4 \cdot 10H_2O$ in 18.60 L of solution

(e) 7.0×10^{-3} mol of I_2 in 100.0 mL of solution

(f) 1.8×10^4 mg of HCl in 0.075 L of solution

23.

Determine the molarity of each of the following solutions:

(a) 1.457 mol KCl in 1.500 L of solution

(b) 0.515 g of H_2SO_4 in 1.00 L of solution

(c) 20.54 g of $Al(NO_3)_3$ in 1575 mL of solution

(d) 2.76 kg of $CuSO_4 \cdot 5H_2O$ in 1.45 L of solution

(e) 0.005653 mol of Br_2 in 10.00 mL of solution

(f) 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution

24.

Consider this question: What is the mass of the solute in 0.500 L of 0.30 *M* glucose, $C_6H_{12}O_6$, used for intravenous injection?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

25.

Consider this question: What is the mass of solute in 200.0 L of a 1.556-*M* solution of KBr?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

26.

Calculate the number of moles and the mass of the solute in each of the following solutions:

(a) 2.00 L of 18.5 *M* H_2SO_4, concentrated sulfuric acid

(b) 100.0 mL of 3.8×10^{-6} *M* NaCN, the minimum lethal concentration of sodium cyanide in blood serum

(c) 5.50 L of 13.3 *M* H_2CO, the formaldehyde used to “fix” tissue samples

(d) 325 mL of 1.8×10^{-6} *M* $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in drinking water

27.

Calculate the number of moles and the mass of the solute in each of the following solutions:

(a) 325 mL of 8.23×10^{-5} *M* KI, a source of iodine in the diet

(b) 75.0 mL of 2.2×10^{-5} *M* H_2SO_4, a sample of acid rain

(c) 0.2500 L of 0.1135 *M* K_2CrO_4, an analytical reagent used in iron assays

(d) 10.5 L of 3.716 *M* $(NH_4)_2SO_4$, a liquid fertilizer

28.

Consider this question: What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

29.

Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

30.

Calculate the molarity of each of the following solutions:

(a) 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum

(b) 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia

(c) 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol

(d) 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C

31.

Calculate the molarity of each of the following solutions:

(a) 293 g HCl in 666 mL of solution, a concentrated HCl solution

(b) 2.026 g $FeCl_3$ in 0.1250 L of a solution used as an unknown in general chemistry laboratories

(c) 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water

(d) 0.0079 g $C_7H_5SNO_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

32.

There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

33.

What volume of a 1.00-*M* $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 *M*?

34.

If 0.1718 L of a 0.3556-*M* C_3H_7OH solution is diluted to a concentration of 0.1222 *M*, what is the volume of the resulting solution?

35.

If 4.12 L of a 0.850 *M*-H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration of the resulting solution?

36.

What volume of a 0.33-*M* $C_{12}H_{22}O_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 *M*?

37.

What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?

38.

What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

(a) 1.00 L of a 0.250-*M* solution of $Fe(NO_3)_3$ is diluted to a final volume of 2.00 L

(b) 0.5000 L of a 0.1222-*M* solution of C_3H_7OH is diluted to a final volume of 1.250 L

(c) 2.35 L of a 0.350-*M* solution of H_3PO_4 is diluted to a final volume of 4.00 L

(d) 22.50 mL of a 0.025-*M* solution of $C_{12}H_{22}O_{11}$ is diluted to 100.0 mL

39.

What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

40.

A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

41.

An experiment in a general chemistry laboratory calls for a 2.00-*M* solution of HCl. How many mL of 11.9 *M* HCl would be required to make 250 mL of 2.00 *M* HCl?

42.

What volume of a 0.20-*M* K_2SO_4 solution contains 57 g of K_2SO_4?

43.

The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ($K_2Cr_2O_7$), what is the maximum permissible molarity of that substance?

44.

Consider this question: What mass of a concentrated solution of nitric acid (68.0% HNO_3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO_3 by mass?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

45.

What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

46.

What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.

47.

What mass of HCl is contained in 45.0 mL of an aqueous HCl solution that has a density of 1.19 g cm^{-3} and contains 37.21% HCl by mass?

48.

The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $CaCO_3$, which is equivalent to milligrams of $CaCO_3$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?

49.

The level of mercury in a stream was suspected to be above the minimum considered safe (1 part per billion by weight). An analysis indicated that the concentration was 0.68 parts per billion. Assume a density of 1.0 g/mL and calculate the molarity of mercury in the stream.

50.

In Canada and the United Kingdom, devices that measure blood glucose levels provide a reading in millimoles per liter. If a measurement of 5.3 m*M* is observed, what is the concentration of glucose ($C_6H_{12}O_6$) in mg/dL?

51.

A throat spray is 1.40% by mass phenol, C_6H_5OH, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.

52.

Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?

53.

A cough syrup contains 5.0% ethyl alcohol, C_2H_5OH, by mass. If the density of the solution is 0.9928 g/mL, determine the molarity of the alcohol in the cough syrup.

54.

D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ($C_6H_{12}O_6$) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.

55.

Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, H_2SO_4, for which the density is 1.3057 g/mL.

This page titled 5.6: Exercises (Solutions and Concentrations) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

5.6.1: Answers to Selected Exercises

1.

(a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

3.

(a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu; (e) 342.297 amu

5.

(a) 56.107 amu;
(b) 54.091 amu;
(c) 199.9976 amu;
(d) 97.9950 amu

8.

(a) % N = 82.24%
% H = 17.76%;
(b) % Na = 29.08%
% S = 40.56%
% O = 30.36%;
(c) % Ca^{2+} = 38.76%

10.

% NH_3 = 38.2%

12.

(a) CS_2
(b) CH_2O

14.

C_6H_6

16.

$Mg_3Si_2H_3O_8$ (empirical formula), $Mg_6Si_4H_6O_{16}$ (molecular formula)

18.

$C_{15}H_{15}N_3$

20.

We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

22.

(a) 0.679 *M*; (b) 1.00 *M*; (c) 0.06998 *M*; (d) 1.75 *M*; (e) 0.070 *M*; (f) 6.6 *M*

24.

(a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 27 g

26.

(a) 37.0 mol H_2SO_4, 3.63×10^3 g H_2SO_4; (b) 3.8×10^{-7} mol NaCN, 1.9×10^{-5} g NaCN; (c) 73.2 mol H_2CO, 2.20 kg H_2CO; (d) 5.9×10^{-7} mol $FeSO_4$, 8.9×10^{-5} g $FeSO_4$

28.

(a) Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) 1.15×10^{-3} *M*

30

30.
(a) 5.04×10^{-3} *M*; (b) 0.499 *M*; (c) 9.92 *M*; (d) 1.1×10^{-3} *M*

32.

0.025 *M*

34.

0.5000 L

36.

1.9 mL

38.

(a) 0.125 *M*; (b) 0.04888 *M*; (c) 0.206 *M*; (d) 0.0056 *M*

40.

11.9 *M*

42.

1.6 L

44.

(a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units: $\%\text{mass}_1 \times \text{mass}_1 = \%\text{mass}_2 \times \text{mass}_2$. This equation can be rearranged to isolate mass_1 and the given quantities substituted into this equation. (b) 58.8 g

46.

114 g

48.

1.75×10^{-3} *M*

50.

95 mg/dL

52.

2.38×10^{-4} mol

54.

0.29 mol

This page titled 5.6.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

5.7: Exercises (Moles and Chemical Formulas)

1.

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?



2.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

3.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

4.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

5.

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

6.

How are electrons and protons similar? How are they different?

7.

How are protons and neutrons similar? How are they different?

8.

Predict and test the behavior of α particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

9.

Predict and test the behavior of α particles fired at a Rutherford atom model.

(a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

10.

In what way are isotopes of a given element always different? In what way(s) are they always the same?

11.

Write the symbol for each of the following ions:

(a) the ion with a 1+ charge, atomic number 55, and mass number 133

(b) the ion with 54 electrons, 53 protons, and 74 neutrons

(c) the ion with atomic number 15, mass number 31, and a 3− charge

(d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

12.

Write the symbol for each of the following ions:

(a) the ion with a 3+ charge, 28 electrons, and a mass number of 71

(b) the ion with 36 electrons, 35 protons, and 45 neutrons

(c) the ion with 86 electrons, 142 neutrons, and a 4+ charge

(d) the ion with a 2+ charge, atomic number 38, and mass number 87

13.

Open the Build an Atom simulation and click on the Atom icon.

(a) Pick any one of the first 10 elements that you would like to build and state its symbol.

(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element.
State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.

(c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.

(d) Predict whether your atom will be stable or unstable. State your reasoning.

(e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

14.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

15.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

16.

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

(a) atomic number 9, mass number 18, charge of 1−

(b) atomic number 43, mass number 99, charge of 7+

(c) atomic number 53, atomic mass number 131, charge of 1−

(d) atomic number 81, atomic mass number 201, charge of 1+

(e) Name the elements in parts (a), (b), (c), and (d).

17.

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

(a) atomic number 26, mass number 58, charge of 2+

(b) atomic number 53, mass number 127, charge of 1−

18.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_{5}\mathrm{B}$

(b) $^{199}_{80}\mathrm{Hg}$

(c) $^{63}_{29}\text{Cu}$

(d) $^{13}_{6}\text{C}$

(e) $^{77}_{34}\text{Se}$

19.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{7}_{3}\text{Li}$

(b) $^{125}_{52}\text{Te}$

(c) $^{109}_{47}\text{Ag}$

(d) $^{15}_{7}\text{N}$

(e) $^{31}_{15}\text{P}$

20.

Click on the site and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

21.

Repeat Exercise 2.20 using an element that has three naturally occurring isotopes.

22.

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

23.

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes, ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

24.

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.

25.

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.00931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

26.

The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

27.

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

28.

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

29.

Write the molecular and empirical formulas of the following compounds:

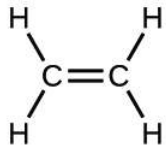
(a)



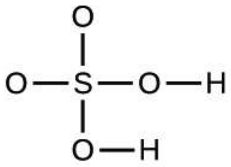
(b)



(c)



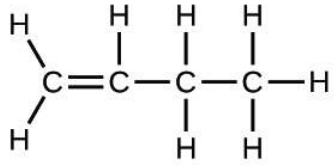
(d)



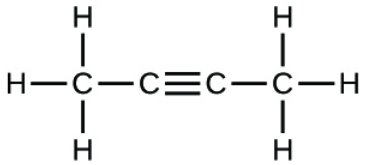
30.

Write the molecular and empirical formulas of the following compounds:

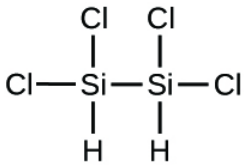
(a)



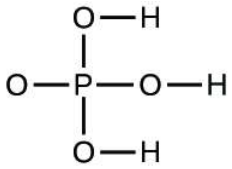
(b)



(c)



(d)



31.

Determine the empirical formulas for the following compounds:

(a) caffeine, $C_8H_{10}N_4O_2$

(b) sucrose, $C_{12}H_{22}O_{11}$

(c) hydrogen peroxide, H_2O_2

(d) glucose, $C_6H_{12}O_6$

(e) ascorbic acid (vitamin C), $C_6H_8O_6$

32.

Determine the empirical formulas for the following compounds:

(a) acetic acid, $C_2H_4O_2$

(b) citric acid, $C_6H_8O_7$

(c) hydrazine, N_2H_4

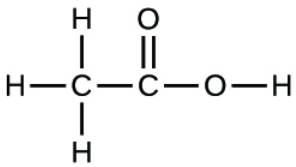
(d) nicotine, $C_{10}H_{14}N_2$

(e) butane, C_4H_{10}

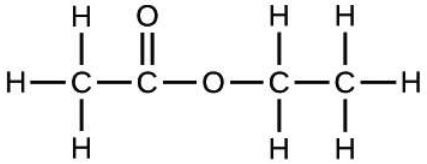
33.

Write the empirical formulas for the following compounds:

(a)



(b)



34.

Open the Build a Molecule simulation and select the “Larger Molecules” tab. Select an appropriate atom's “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound?

35.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with two carbons, six hydrogens, and one oxygen.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

36.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with three carbons, seven hydrogens, and one chlorine.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

37.

Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

38.

Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

39.

Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.

40.

Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol (C_2H_5OH), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.

41.

How are the molecular mass and the molar mass of a compound similar and how are they different?

42.

Calculate the molar mass of each of the following compounds:

(a) hydrogen fluoride, HF

(b) ammonia, NH_3

(c) nitric acid, HNO_3

(d) silver sulfate, Ag_2SO_4

(e) boric acid, $B(OH)_3$

43.

Calculate the molar mass of each of the following:

(a) S_8

(b) C_5H_{12}

(c) $Sc_2(SO_4)_3$

(d) CH_3COCH_3 (acetone)

(e) $C_6H_{12}O_6$ (glucose)

44.

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

(a) limestone, $CaCO_3$

(b) halite, NaCl

(c) beryl, $Be_3Al_2Si_6O_{18}$

(d) malachite, $Cu_2(OH)_2CO_3$

(e) turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

45.

Calculate the molar mass of each of the following:

(a) the anesthetic halothane, $C_2HBrClF_3$

(b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$

(c) caffeine, $C_8H_{10}N_4O_2$

(d) urea, $CO(NH_2)_2$

(e) a typical soap, $C_{17}H_{35}CO_2Na$

46.

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

47.

Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) 1.6×10^{-3} mol $Na_2\ SO_4$

(d) 6.854×10^3 mol glucose, $C_6\ H_{12}\ O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

48.

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

(a) 2.12 g of potassium bromide, KBr

(b) 0.1488 g of phosphoric acid, H_3PO_4

(c) 23 kg of calcium carbonate, $CaCO_3$

(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$

(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

49.

Determine the mass of each of the following:

(a) 2.345 mol LiCl

(b) 0.0872 mol acetylene, C_2H_2

(c) 3.3×10^{-2} mol $Na_2\ CO_3$

(d) 1.23×10^3 mol fructose, $C_6\ H_{12}\ O_6$

(e) 0.5758 mol $FeSO_4(H_2O)_7$

50.

The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?

51.

Determine the mass in grams of each of the following:

(a) 0.600 mol of oxygen atoms

(b) 0.600 mol of oxygen molecules, O_2

(c) 0.600 mol of ozone molecules, O_3

52.

A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

53.

Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, $ZrSiO_4$, a semiprecious stone.

54.

Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4, 0.6 mol of C_6H_6, or 0.4 mol of C_3H_8.

55.

Determine which of the following contains the greatest mass of aluminum: 122 g of $AlPO_4$, 266 g of Al_2Cl_6, or 225 g of Al_2S_3.

56.

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

57.

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

58.

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

59.

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

60.

A tube of toothpaste contains 0.76 g of sodium monofluorophosphate (Na_2PO_3F) in 100 mL.

(a) What mass of fluorine atoms in mg was present?

(b) How many fluorine atoms were present?

61.

Which of the following represents the least number of molecules?

(a) 20.0 g of H_2O (18.02 g/mol)

(b) 77.0 g of CH_4 (16.06 g/mol)

(c) 68.0 g of C_3H_6 (42.08 g/mol)

(d) 100.0 g of N_2O (44.02 g/mol)

(e) 84.0 g of HF (20.01 g/mol)

This page titled 5.7: Exercises (Moles and Chemical Formulas) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

5.7.1: Answers to Selected Exercises (Moles and Chemical Formulas)

1.

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

3.

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

5.

Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

7.

Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

9.

(a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

11.

(a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

13.

(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

15.

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or $_{3}^{6}\mathbf{Li}$. (b) $^{6}Li^{+}$ or msubsupmsubsupmsupmsup

17.

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

19.

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

21.

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of

Ne-21. The average mass would be 20.18 amu. Checking the nature's mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

23.

79.90 amu

25.

Turkey source: 20.3% (of 10.0129 amu isotope); US source: 19.1% (of 10.0129 amu isotope)

27.

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

29.

(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

31.

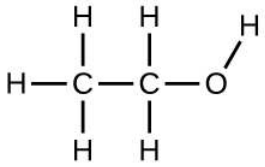
(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

33.

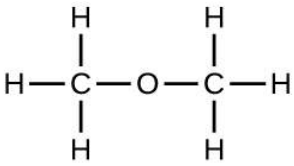
(a) CH_2O; (b) C_2H_4O

35.

(a) ethanol



(b) methoxymethane, more commonly known as dimethyl ether



(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

37.

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

39.

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

41.

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

43.

(a) 256.48 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}

45.

(a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}

47.

(a) 0.819 g;
(b) 307 g;
(c) 0.23 g;
(d) 1.235×10^6 g (1235 kg);
(e) 765 g

49.

(a) 99.41 g;
(b) 2.27 g;
(c) 3.5 g;
(d) 222 kg;
(e) 160.1 g

51.

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

53.

zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g

55.

$AlPO_4$: 1.000 mol or 26.98 g Al
Al_2Cl_6: 1.994 mol or 53.74 g Al
Al_2S_3: 3.00 mol or 80.94 g Al
The Al_2S_3 sample thus contains the greatest mass of Al.

57.

3.113×10^{25} C atoms

59.

0.865 servings, or about 1 serving.

61.

20.0 g H_2O represents the least number of molecules since it has the least number of moles.

This page titled 5.7.1: Answers to Selected Exercises (Moles and Chemical Formulas) is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

6: Gases and the Ideal Gas Law

6.1: Gas Pressure

6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

6.2.1: Molar Mass of a Gas and Dalton's Law

6.2.2: The Kinetic-Molecular Theory

6.3: Exercises

6.3.1: Answers to Selected Exercises

This page titled 6: Gases and the Ideal Gas Law is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

6.1: Gas Pressure

Learning Objectives

By the end of this section, you will be able to:

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure **6.1.1**). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

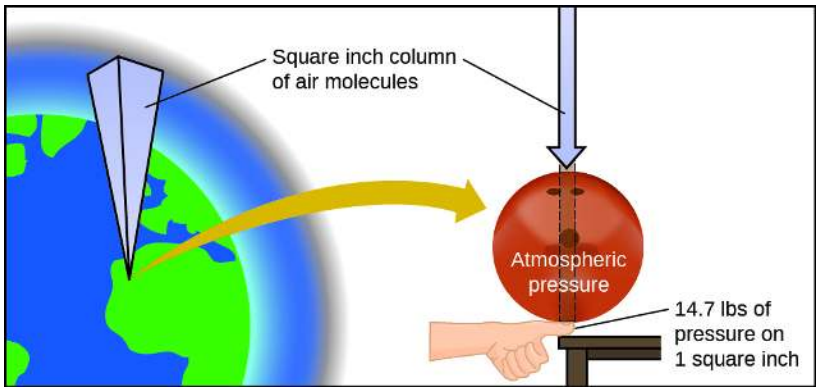


Figure **6.1.1**: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Link to Learning

A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

A smaller scale demonstration of this phenomenon is briefly explained.

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

In general, **pressure** is defined as the force exerted on a given area: (P= F/A). Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which exerts a greater pressure in Figure **6.1.2** —the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot } = 14,000\frac{lb}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250in^2} = 14lb/in^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade } = 120\frac{lb}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 lb/in^2$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure. On the other hand, if the skater removes their skates and stands with bare feet (or regular footwear) on the ice, the larger area over which their weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot } = 120\frac{lb}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 in^2} = 2 lb/in^2$$



Figure **6.1.2**: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of the skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or **bar** (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere** (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table **6.1.1** provides some information on these and a few other common units for pressure measurements

Table **6.1.1**: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m^2 recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi
atmosphere (atm)	1 atm = 101,325 Pa = 760 torr air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly) commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa used by aviation industry, also some weather reports
torr	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

Example 6.1.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 6.1.1.

a. $$29.2 \text{ in } Hg_g \times \frac{25.4mm}{1im} \times \frac{1 \text{ torr}}{1mmHg_g} = 742 \text{ torr}$$

b. $$742 \text{ torr } \times \frac{1atm}{760 \text{ torr}} = 0.976atm$$

c. $$742 \text{ torr } \times \frac{101.325kPa}{760 \text{ torr}} = 98.9kPa$$

d. $$98.9kPa \times \frac{1000Pa}{1kPa} \times \frac{1bar}{100,000Pa} \times \frac{1000mbar}{1bar} = 989mbar$$

Exercise 6.1.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure 6.1.3). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

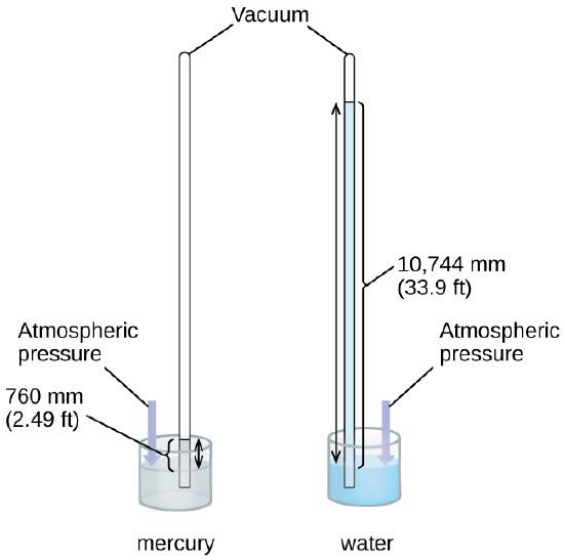


Figure **6.1.3**: In a barometer, the height, *h*, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be Extra close brace or missing open brace as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The **torr** was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. A **manometer** is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure **6.1.4**) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

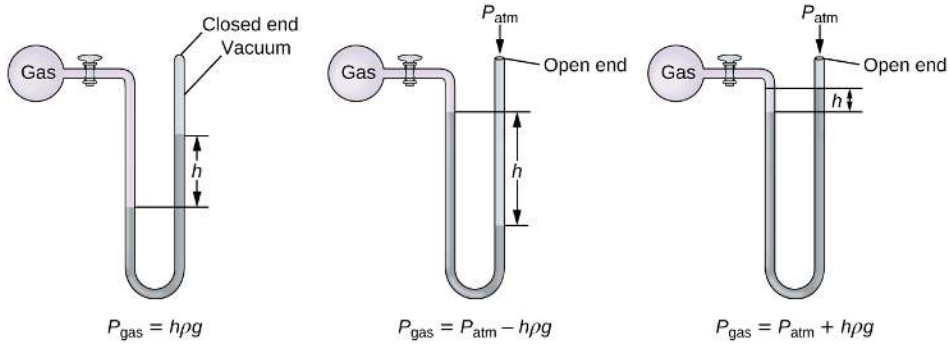


Figure **6.1.4**: A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (*h*) is a measure of the pressure. Mercury is usually used because of its large density.

Chemistry in Everyday Life: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure **6.1.5**). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated

until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



Figure **6.1.5**: (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

How Sciences Interconnect: Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure **6.1.6**) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

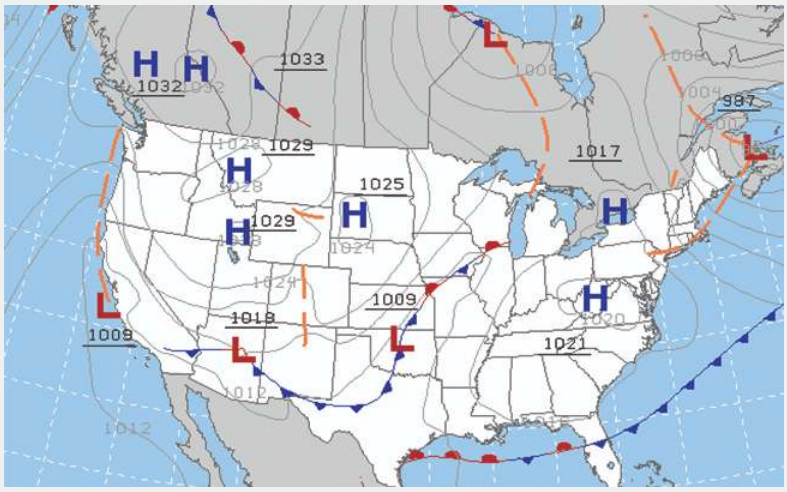


Figure **6.1.6**: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure **6.1.7** the

exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

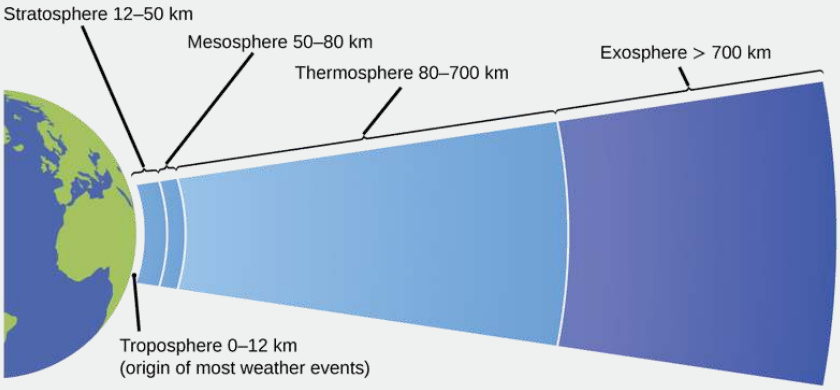


Figure **6.1.7**: Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

This page titled 6.1: Gas Pressure is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **9.1: Gas Pressure** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

Learning Objectives

By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure **6.2.1**), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

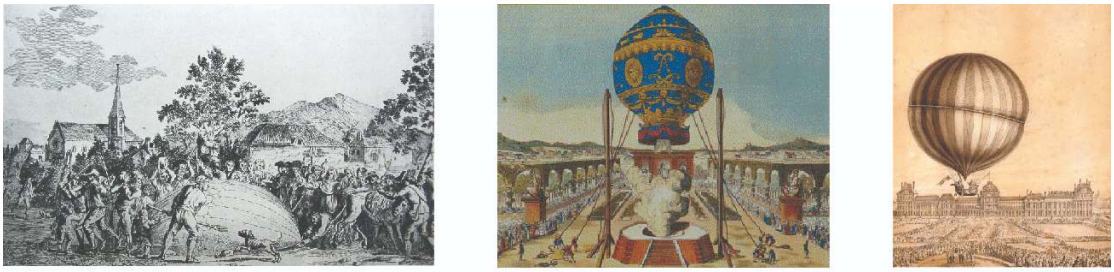


Figure **6.2.1**: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

6.2.1: Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure **6.2.2**) and the pressure increases.

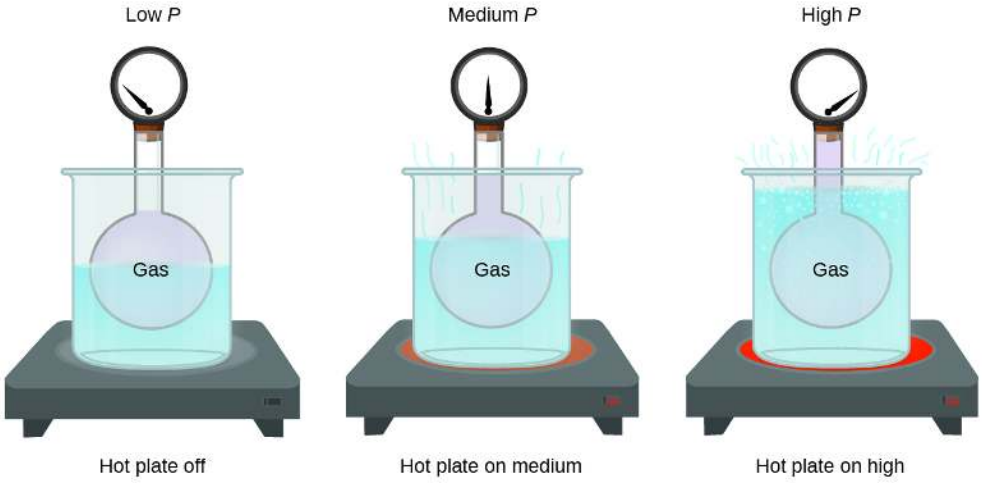


Figure **6.2.2**: The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure **6.2.3**. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
−100	173	36.0
−50	223	46.4
0	273	56.7
50	323	67.1
100	373	77.5
150	423	88.0

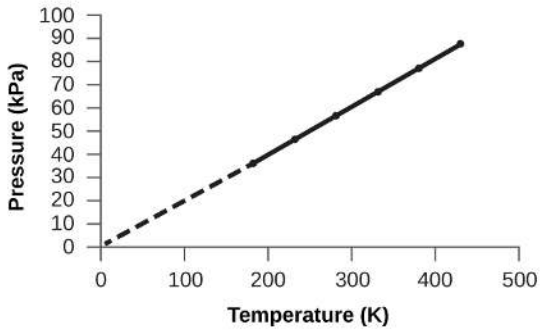


Figure **6.2.3**: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the P-T relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{ constant } \times T \text{ or } P = k \times T$$

where $\propto$ means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the $\frac{P}{T}$ ratio is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$ which reduces to

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

✔ Example 6.2.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the

unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{K}}}{297 \cancel{\text{K}}} = 390 \text{ kPa}$$

? Exercise 6.2.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 torr

6.2.2: Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

Link to Learning

This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure 9.12.

Temperature (°C)	Temperature (K)	Volume (L)
–3	270	22
–23	250	21
–53	220	18
–162	111	9

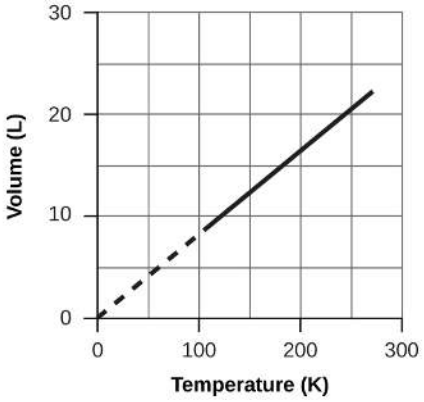


Figure 9.12 The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant.*

Mathematically, this can be written as:

$$V \alpha T \text{ or } V = \text{ constant } \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the P-T relationship, this leads to another form of Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}. \tag{6.2.1}$$

Example 6.2.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300L}{283K} = \frac{V_2}{303K}$$

Rearranging and solving gives:

$$V_2 = \frac{0.300L \times 303 \cancel{K}}{283 \cancel{K}} = 0.321 \text{ L}$$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 6.2.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

Example 6.2.3: Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0cm^3}{273.15K} = \frac{131.7cm^3}{T_2}$$

Rearrangement gives

$$T_2 = \frac{131.7 \cancel{cm^3} \times 273.15 \text{ K}}{150.0 \cancel{cm^3}} = 239.8 \text{ K}$$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

? Exercise 6.2.3

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

6.2.3: Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure **6.2.4**.

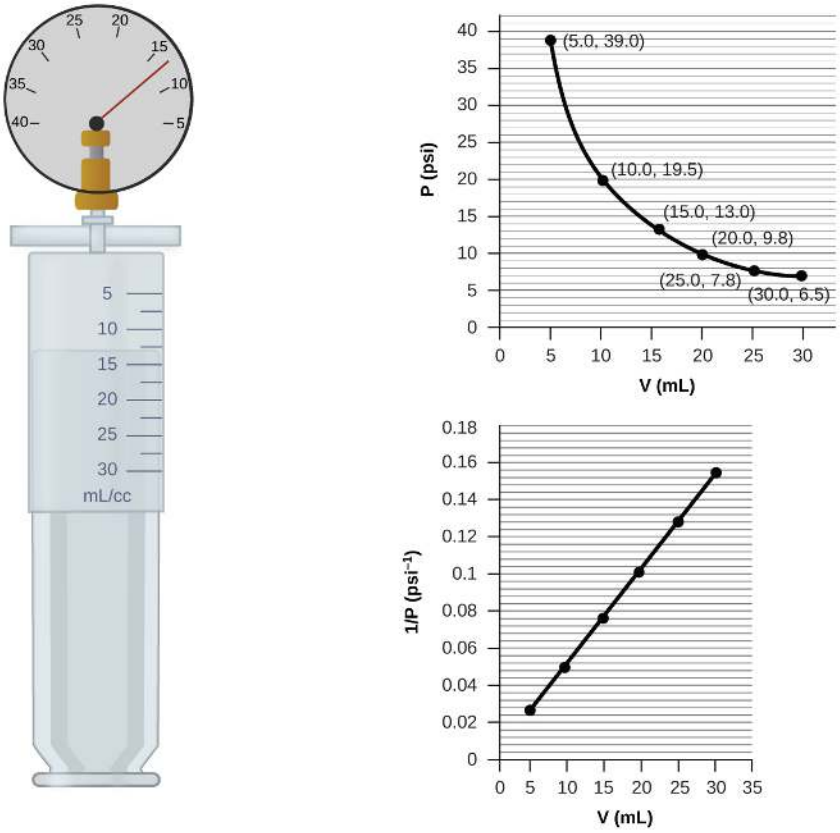


Figure **6.2.4**: When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

Unlike the P-T and V-T relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto \frac{1}{V} \tag{6.2.2}$$

or

$$P = k \cdot \frac{1}{V} \tag{6.2.3}$$

or

$$P \cdot V = k \tag{6.2.4}$$

or

$$P_1V_1 = P_2V_2 \tag{6.2.5}$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure

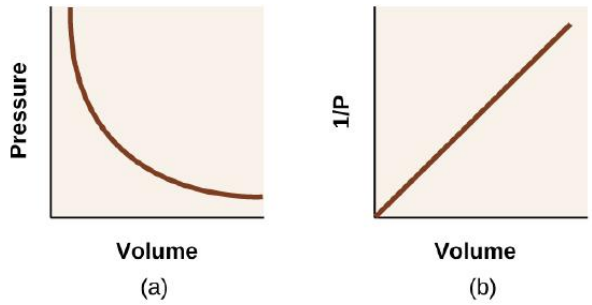


Figure **6.2.5**: The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $\frac{1}{P}$ vs. V is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example 6.2.4: Volume of a Gas Sample

The sample of gas in Figure **6.2.4**: has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the P-V graph in Figure **6.2.5**
b. the $\frac{1}{P}$ vs. V graph in Figure **6.2.5**
c. the Boyle's law equations (Equations 6.2.2 - 6.2.5)

Comment on the likely accuracy of each method.

Solution

(a) Estimating from the P-V graph gives a value for P somewhere around 27 psi.

(b) Estimating from the \frac{1}{P}\) versus V graph give a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume (PV) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1\ V_1 = P_2\ V_2$$
$$(13.0\ \text{psi}) \times (15.0\ \text{mL} = P_2 \times (7.5\ \text{mL})$$

Solving:

$$P_2 = \frac{13.0\ \text{psi} \times 15.0\ \cancel{\text{mL}}}{7.5\ \cancel{\text{mL}}} = 26\ \text{psi}$$

It was more difficult to estimate well from the P-V graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Exercise 6.2.4

The sample of gas in Figure **6.2.4** has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure **6.2.5**
b. the $\frac{1}{P}$ vs. \(*V*\) graph in Figure **6.2.5**
c. the Boyle's law equations (6.2.2 - 6.2.5)

Comment on the likely accuracy of each method.

Answer

(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Chemistry in Everyday Life: Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure **6.2.6**).

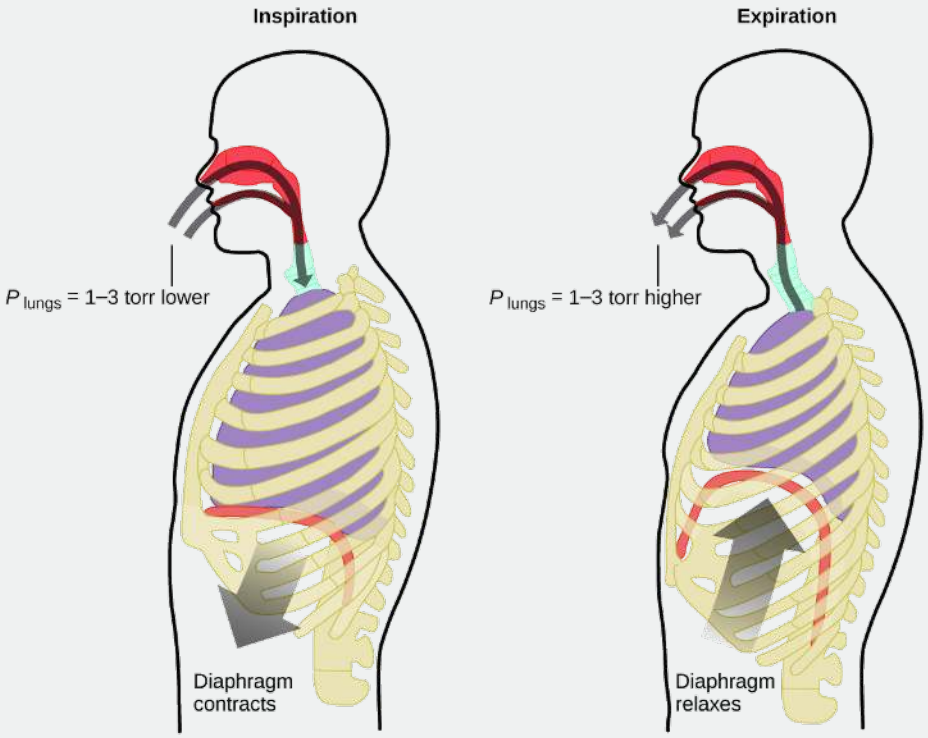


Figure **6.2.6**: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

6.2.4: Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$V \propto n \tag{6.2.6}$$

or

$$V = k \times n \tag{6.2.7}$$

or

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \tag{6.2.8}$$

Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.

Link to Learning

Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

6.2.5: The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's law: $\frac{P}{T}$ = constant at constant V and n
- Charles's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} K^{-1}.

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 6.2.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

We must rearrange $PV = nRT$ to solve for V:

$$V = \frac{nRT}{P}$$

If we choose to use R = 0.08206 L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the "right" units:

$$n = 655 \text{ g } CH_4 \times \frac{1 \text{ mol}}{16.043 \text{ g } CH_4} = 40.8 \text{ mol}$$

$$T = 25°C + 273 = 298 \text{ K}$$

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \text{ mol})\left(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}\right)(298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Exercise 6.2.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the **combined gas law** is obtained:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

using units of atm, L, and K. Both sets of conditions are equal to the product of n R (where n = the number of moles of the gas and R is the ideal gas law constant).

Example 6.2.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure **6.2.7**). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Figure 6.2.7: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \rightarrow \frac{(153atm)(13.2L)}{(300K)} = \frac{(3.13atm)\,(V_2)}{(310K)}$$

Solving for V_2:

$$V_2 = \frac{(153\text{ atm }\,)(13.2L)(310K)}{(300K)(3.13\text{ atm }\,)} = 667L$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good “ballpark” estimate.)

? Exercise 6.2.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

Chemistry in Everyday Life: The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 6.2.8) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure **6.2.8**: Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in their BCD expands because of lower pressure according to Boyle’s law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and they begin to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

6.2.6: Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa).[1] At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (Figure **6.2.9**).

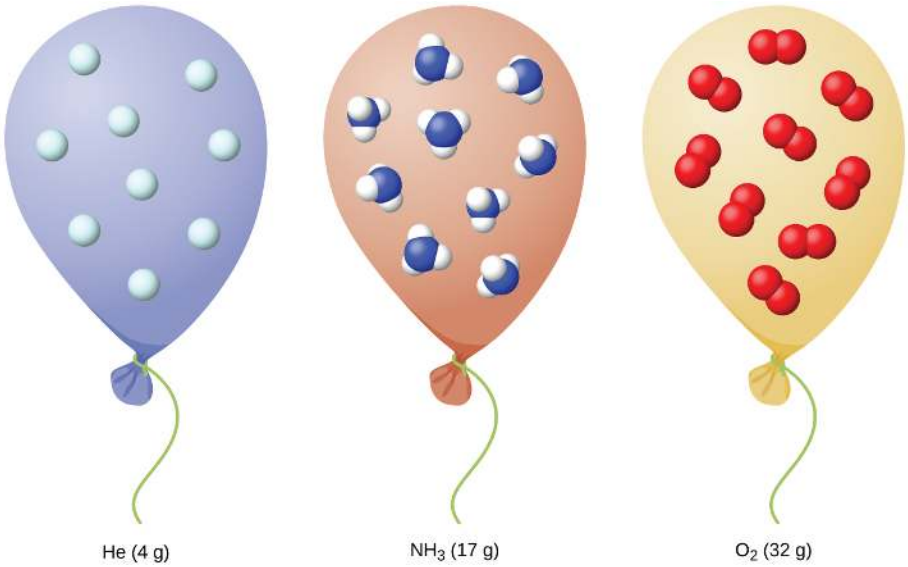


Figure **6.2.9**: Regardless of its chemical identity, one mole of gas behaving ideally occupies a volume of ~22.4 L at STP.

6.2.7: Footnotes

- 1The IUPAC definition of standard pressure was changed from 1 atm to 1 bar (100 kPa) in 1982, but the prior definition remains in use by many literature resources and will be used in this text.

This page titled 6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **9.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.2.1: Molar Mass of a Gas and Dalton's Law

Learning Objectives

By the end of this section, you will be able to:

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton’s law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the “father of modern chemistry,” changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, “It took the mob only a moment to remove his head; a century will not suffice to reproduce it.”[2] Much of the knowledge we do have about Lavoisier's contributions is due to his wife, Marie-Anne Paulze Lavoisier, who worked with him in his lab. A trained artist fluent in several languages, she created detailed illustrations of the equipment in his lab, and translated texts from foreign scientists to complement his knowledge. After his execution, she was instrumental in publishing Lavoisier's major treatise, which unified many concepts of chemistry and laid the groundwork for significant further study.

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask “How much?” The essential property involved in such use of stoichiometry is the amount of substance, typically measured in moles (n). For gases, molar amount can be derived from convenient experimental measurements of pressure, temperature, and volume. Therefore, these measurements are useful in assessing the stoichiometry of pure gases, gas mixtures, and chemical reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts already discussed.

6.2.1.1: Gas Density and Molar Mass

The ideal gas law described previously in this chapter relates the properties of pressure P, volume V, temperature T, and molar amount n. This law is universal, relating these properties in identical fashion regardless of the chemical identity of the gas:

$$PV = nRT$$

The density d of a gas, on the other hand, is determined by its identity. As described in another chapter of this text, the density of a substance is a characteristic property that may be used to identify the substance.

$$d = \frac{m}{V}$$

Rearranging the ideal gas equation to isolate V and substituting into the density equation yields

$$d = \frac{mP}{nRT} = \left(\frac{m}{n}\right)\frac{P}{RT}$$

The ratio m/n is the definition of molar mass, $\mathcal{M}$:

$$\mathcal{M} = \frac{m}{n}$$

The density equation can then be written

$$d = \frac{\mathcal{M}P}{RT}$$

This relation may be used for calculating the densities of gases of known identities at specified values of pressure and temperature as demonstrated in Example **6.2.1.1**.

Example 6.2.1.1: Measuring Gas Density

What is the density of molecular nitrogen gas at STP?

Solution

The molar mass of molecular nitrogen, N_2, is 28.01 g/mol. Substituting this value along with standard temperature and pressure into the gas density equation yields

$$d = \frac{\mathcal{M}P}{RT} = \frac{(28.01\ \text{g/mol})(1.00\ \text{atm})}{(0.0821\ \text{L}\cdot\text{atm}\cdot\text{mol}^{-1}\text{K}^{-1})(273\ \text{K})} = 1.25\ \text{g / L}$$

Exercise 6.2.1.1

What is the density of molecular hydrogen gas at 17.0 °C and a pressure of 760 torr?

Answer

d = 0.0847 g/L

When the identity of a gas is unknown, measurements of the mass, pressure, volume, and temperature of a sample can be used to calculate the molar mass of the gas (a useful property for identification purposes). Combining the ideal gas equation

$$PV = nRT$$

and the definition of molar mass

$$\mathcal{M} = \frac{m}{n}$$

yields the following equation:

$$\mathcal{M} = \frac{mRT}{PV}$$

Determining the molar mass of a gas via this approach is demonstrated in Example **6.2.1.2**.

Example 6.2.1.2: Determining the Molecular Formula of a Gas from its Molar Mass and Empirical Formula

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

First determine the empirical formula of the gas. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen.

$$85.7\ \text{g}\ C \times \frac{1\ \text{mol}\ C}{12.01\ \text{g}\ C} = 7.136\ \text{mol}\ C$$

$$14.3\ \text{g}\ H \times \frac{1\ \text{mol}\ H}{1.01\ \text{g}\ H} = 14.158\ \text{mol}\ H$$

In the last step, realize that the smallest whole number ratio is the empirical formula:

$$\frac{7.136}{7.136} = 1.00\ \text{mol}\ C$$

$$\frac{14.158}{7.136} = 1.98\ \text{mol}\ H$$

Empirical formula is $\mathbf{CH_2}$ [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the provided values for mass, pressure, temperature and volume to compute the molar mass of the gas:

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(1.56\text{ g})\left(0.0821\text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\text{K}^{-1}\right)(323\text{ K})}{(0.984\text{ atm})(1.00\text{ L})} = 42.0\text{ g/mol}$$

Comparing the molar mass to the empirical formula mass shows how many empirical formula units make up a molecule:

$$\frac{\mathcal{M}}{EM} = \frac{42.0\text{ g/mol}}{14.0\text{ g/mol}} = 3$$

The molecular formula is thus derived from the empirical formula by multiplying each of its subscripts by three:

$$(CH_2)_3 = C_3H_6$$

Exercise 6.2.1.2

Acetylene, a fuel used welding torches, is composed of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer

Empirical formula, CH; Molecular formula, C_2H_2

Example 6.2.1.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see Figure 6.2.1.1)

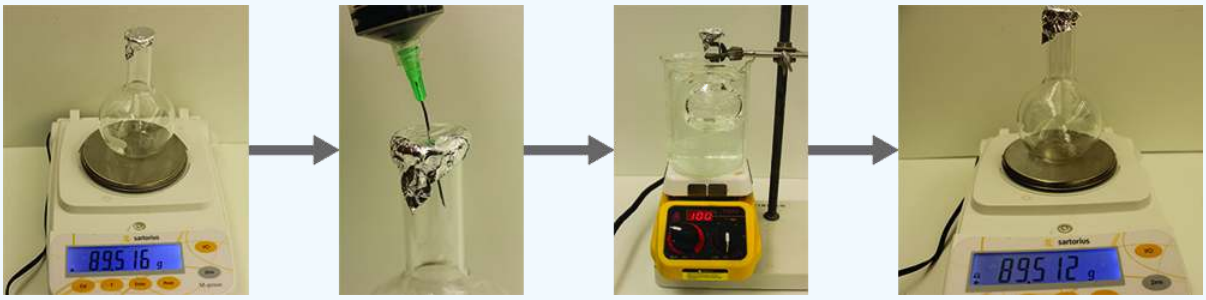


Figure 6.2.1.1: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since $\mathcal{M} = \frac{m}{n}$ and $n = \frac{PV}{RT}$ substituting and rearranging gives $\mathcal{M} = \frac{mRT}{PV}$,

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494\text{ g}) \times 0.08206\text{ L}\cdot\text{atm/mol K} \times 372.8\text{ K}}{0.976\text{ atm} \times 0.129\text{ L}} = 120\text{ g/mol}$$

? Exercise 6.2.1.3

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer

124 g/mol P_4

6.2.1.2: The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure **6.2.1.2**). The pressure exerted by each individual gas in a mixture is called its **partial pressure**. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{\text{Total}} = P_A + P_B + P_C + \ldots = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

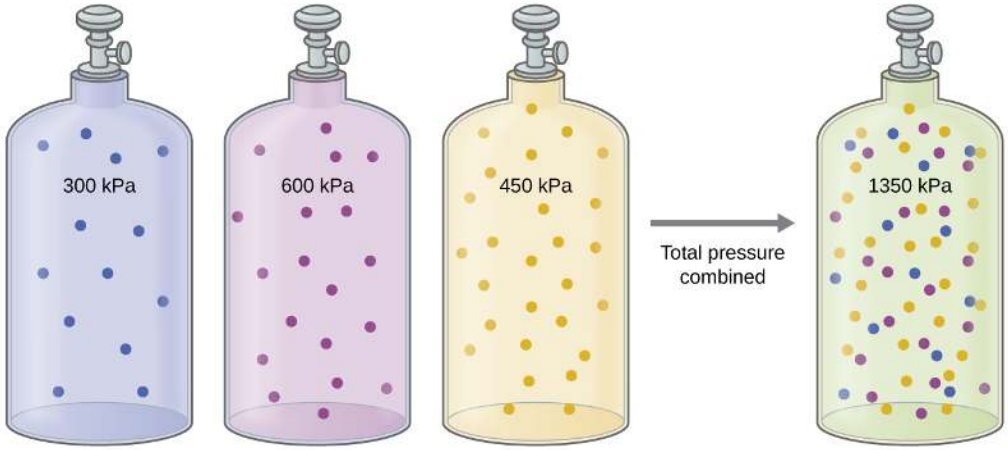


Figure **6.2.1.2**: If equal-volume cylinders containing gasses at pressures of 300 kPa, 450 kPa, and 600 kPa are all combined in the same-size cylinder, the total pressure of the gas mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction** (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{\text{Total}}$$

where

$$X_A = \frac{n_A}{n_{\text{Total}}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

✓ Example 6.2.1.4: The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50 10^{-3} mol of H_2, 1.00 10^{-3} mol of He, and 3.00 10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{H_2} = \frac{\left(2.50 \times 10^{-3}\ \cancel{\text{mol}}\right)\left(0.08206\ \cancel{\text{L}}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}}\right)(308\ \cancel{\text{K}})}{10.0\ \cancel{\text{L}}} = 6.32 \times 10^{-3}\ \text{atm}$$

$$= \frac{\left(1.00 \times 10^{-3}\ \cancel{\text{mol}}\right)\left(0.08206\ \cancel{\text{L}}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}}\right)(308\ \cancel{\text{K}})}{10.0\ \cancel{\text{L}}} = 2.53 \times 10^{-3}\ \text{atm}$$

$$= \frac{\left(3.00 \times 10^{-4}\ \cancel{\text{mol}}\right)\left(0.08206\ \cancel{\text{L}}\ \text{atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}}\right)(308\ \cancel{\text{K}})}{10.0\ \cancel{\text{L}}} = 7.58 \times 10^{-4}\ \text{atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076)\ \text{atm} = 9.61 \times 10^{-3}\ \text{atm}$$

Exercise 6.2.1.4

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

Example 6.2.1.5: The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, $\mathbf{O_2}$, and 8.41 mol nitrous oxide, $\mathbf{N_2O}$. The total pressure of the mixture is 192 kPa.

a. What are the mole fractions of O_2 and N_2O?
b. What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by $X_A = \frac{n_A}{n_{\text{Total}}}$ and the partial pressure is $P_A = X_A P_{Total}$.

For $\mathbf{O_2}$,

$$X_{O_2} = \frac{n_{O_2}}{n_{\text{Total}}} = \frac{2.83 mol}{(2.83 + 8.41) mol} = 0.252$$

and $P_{O_2} = X_{O_2} \times P_{\text{Total}} = 0.252 \times 192 kPa = 48.4 kPa$

For $\mathbf{N_2O}$,

$$X_{N_2O} = \frac{n_{N_2O}}{n_{\text{Total}}} = \frac{8.41 mol}{(2.83 + 8.41) mol} = 0.748$$

and

$$P_{N_2O} = X_{N_2O} \times P_{\text{Total}} = 0.748 \times 192 kPa = 144 kPa$$

? Exercise 6.2.1.5

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer

1.87 atm

6.2.1.3: Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure **6.2.1.3**), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

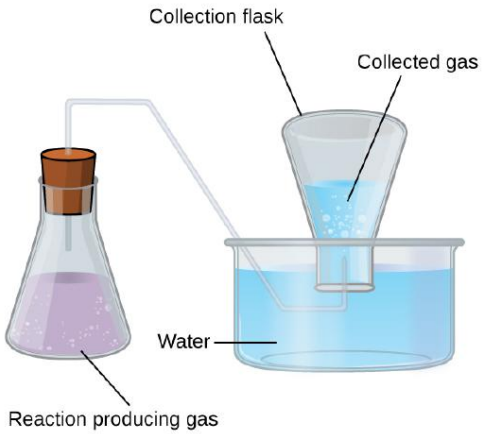


Figure **6.2.1.3**: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the "dry" gas pressure, that is, the pressure of the gas only, without water vapor. The **vapor pressure of water**, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure **6.2.1.4**); more detailed information on the temperature dependence of water vapor can be found in Table **6.2.1.1**, and vapor pressure will be discussed in more detail in the next chapter on liquids.

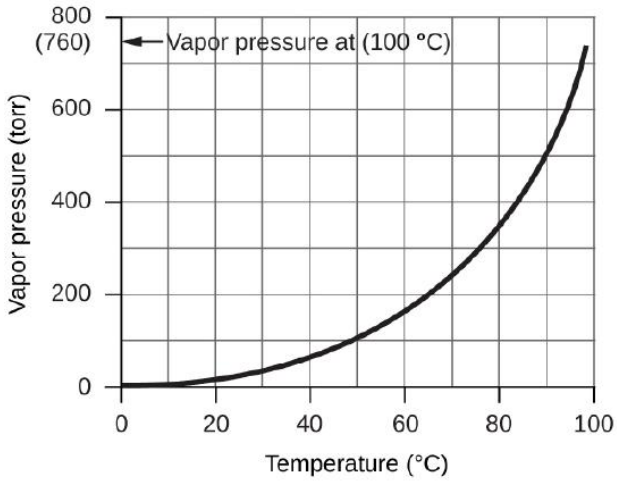


Figure **6.2.1.4**: This graph shows the vapor pressure of water at sea level as a function of temperature.

Table **6.2.1.1**: Vapor Pressure of Ice and Water in Various Temperatures at Sea Level

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
–10	1.95	18	15.5	30	31.8
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

Example **6.2.1.6**: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure **6.2.1.3**, what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{Ar} + P_{H_2O}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{Ar} = P_T - P_{H_2O}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{Ar} = 750 \text{ torr } - 25.2 \text{ torr } = 725 \text{ torr}$$

? Exercise 6.2.1.6

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen from this sample have under the same conditions of temperature and pressure?

Answer

0.537 L

6.2.1.4: Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions.

We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

6.2.1.5: Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)}$$

a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure **6.2.1.5**. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

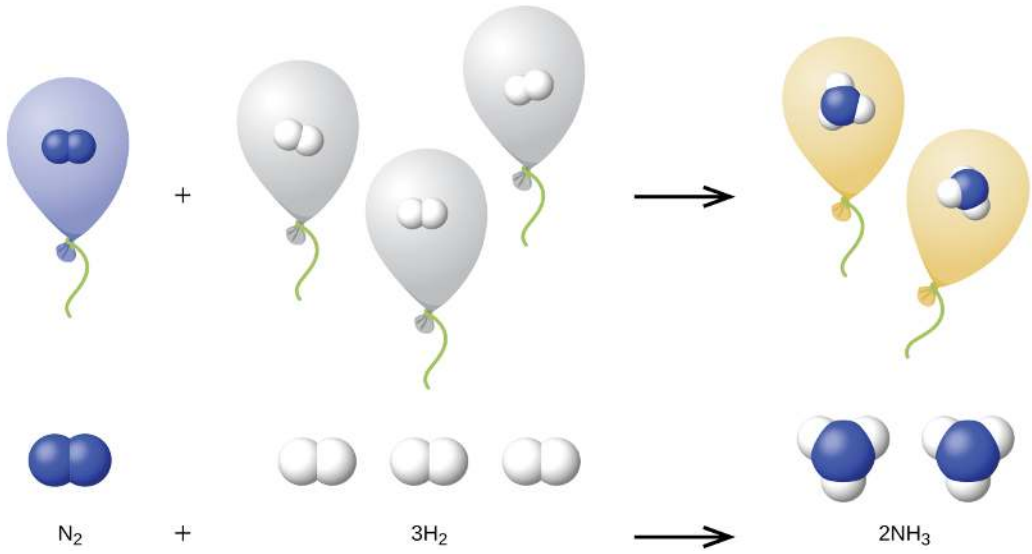


Figure **6.2.1.5**: One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.

Example 6.2.1.7: Reaction of Gases

Propane, $\mathbf{C_3H_8\,(g)}$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\underset{\mathbf{C_3H_8\,(g)+5\,O_2\,(g)}}{\mathbf{1\ volume + 5\ volumes}} \longrightarrow \underset{\mathbf{3\,CO_2\,(g)+4\,H_2O\,(l)}}{\mathbf{3\ volumes + 4\ volumes}}$$

From the equation, we see that one volume of $\mathbf{C_3H_8}$ will react with five volumes of $\mathbf{O_2}$:

$$2.7\ \cancel{L}\ \mathbf{C_3H_8} \times \frac{\mathbf{5\ L\ O_2}}{\mathbf{1\ \cancel{L}C_3H_8}} = \mathbf{13.5\ L\ O_2}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 6.2.1.7

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00 10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

Answer

3.34 tanks (2.34 10^4 L)

Example 6.2.1.8: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$\mathbf{N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)}$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683 \text{ billion } ft^3 NH_3 \times \frac{3 \text{ billion } ft^3 H_2}{2 \text{ billion } ft^3 NH_3} = 1.02 \times 10^3 \text{ billion } ft^3 H_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

? Exercise 6.2.1.8

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer

51.0 L

✓ Example 6.2.1.9: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\,Ga\,(s) + 6\,HCl\,(aq) \longrightarrow 2\,GaCl_3\,(aq) + 3\,H_2\,(g)$$

Solution

Convert the provided mass of the limiting reactant, Ga, to moles of hydrogen produced:

$$8.88 \cancel{\text{ g Ga}} \times \frac{1 \cancel{\text{ mol Ga}}}{69.723 \cancel{\text{ g Ga}}} \times \frac{3 \text{ mol } H_2}{2 \cancel{\text{ mol Ga}}} = 0.191 \text{ mol } H_2$$

Convert the provided temperature and pressure values to appropriate units (K and atm, respectively), and then use the molar amount of hydrogen gas and the ideal gas equation to calculate the volume of gas:

$$V = \left(\frac{nRT}{P}\right) = \frac{0.191 \cancel{\text{ mol}} \times 0.08206 \text{ L } \cancel{\text{atm mol}^{-1}} \text{K}^{-1} \times 300 \text{ K}}{0.951 \cancel{\text{ atm}}} = 4.94 \text{ L}$$

? Exercise 6.2.1.9

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in excess oxygen?

Answer

1.30 10^3 L

How Sciences Interconnect: Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. Most if this IR radiation, however, is absorbed by certain atmospheric gases, effectively trapping heat within the atmosphere in a phenomenon known as the greenhouse effect. This effect maintains global temperatures within the range needed to sustain life on earth. Without our atmosphere, the

earth's average temperature would be lower by more than 30 °C (nearly 60 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 6.2.1.6).

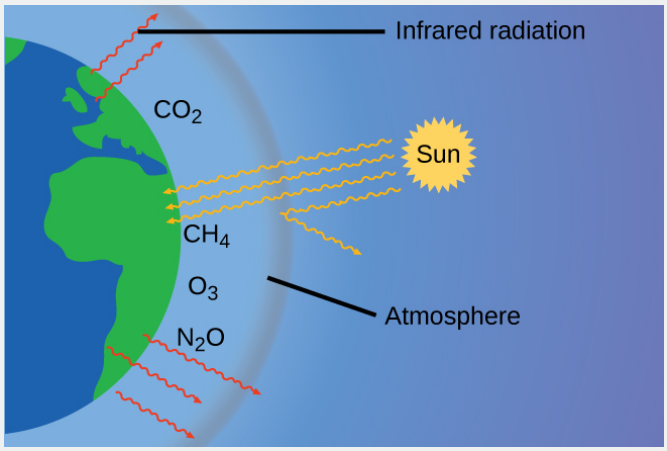


Figure 6.2.1.6: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO2. Reliable data from ice cores reveals that CO2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO2 concentration has increased preindustrial levels of ~280 ppm to more than 400 ppm today (Figure 6.2.1.7).

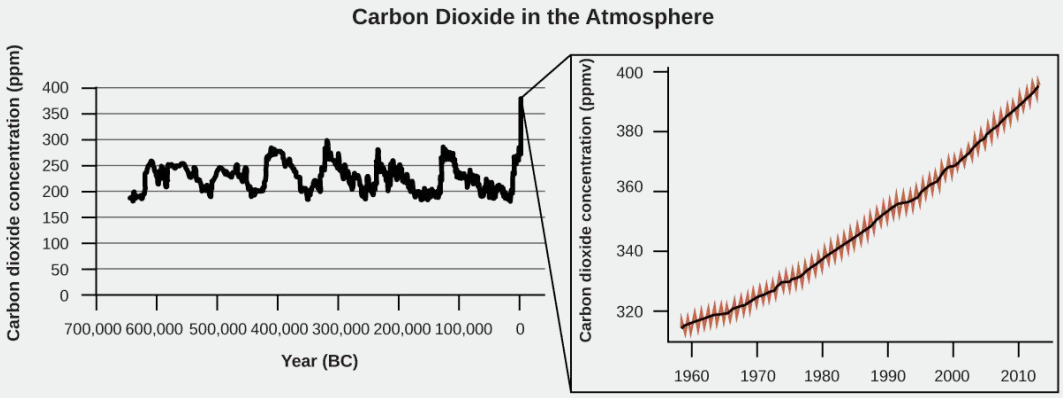


Figure 6.2.1.7: CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Link to Learning

Click here to see a 2-minute video explaining greenhouse gases and global warming.

Portrait of a Chemist: Susan Solomon

Atmospheric and climate scientist Susan Solomon (Figure 6.2.1.8) is the author of one of *The New York Times* books of the year (*The Coldest March*, 2001), one of Time magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica, and has authored many important papers on climate change. She has been awarded the top scientific honors in the US and France (the National Medal of Science and the Grande Medaille, respectively), and is a member of the National Academy of Sciences, the Royal Society, the French

Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT, and continues to work at NOAA.



Figure **6.2.1.8**: Susan Solomon's research focuses on climate change and has been instrumental in determining the cause of the ozone hole over Antarctica. (credit: National Oceanic and Atmospheric Administration)

For more information, watch this video about Susan Solomon.

6.2.1.6: Footnotes

- 2"Quotations by Joseph-Louis Lagrange," last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.../Lagrange.html

---

This page titled 6.2.1: Molar Mass of a Gas and Dalton's Law is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **9.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.2.2: The Kinetic-Molecular Theory

Learning Objectives

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

6.2.2.1: The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure **6.2.2.1**).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume volume of a given amount of gas at a given temperature is decreased (that is, if the gas is *compressed*), the molecules will be exposed to a decreased container wall area. Collisions with the container wall will therefore occur more frequently and the pressure exerted by the gas will increase (Figure **6.2.2.1**).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure **6.2.2.1**).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the

(partial) pressures of the individual gases.

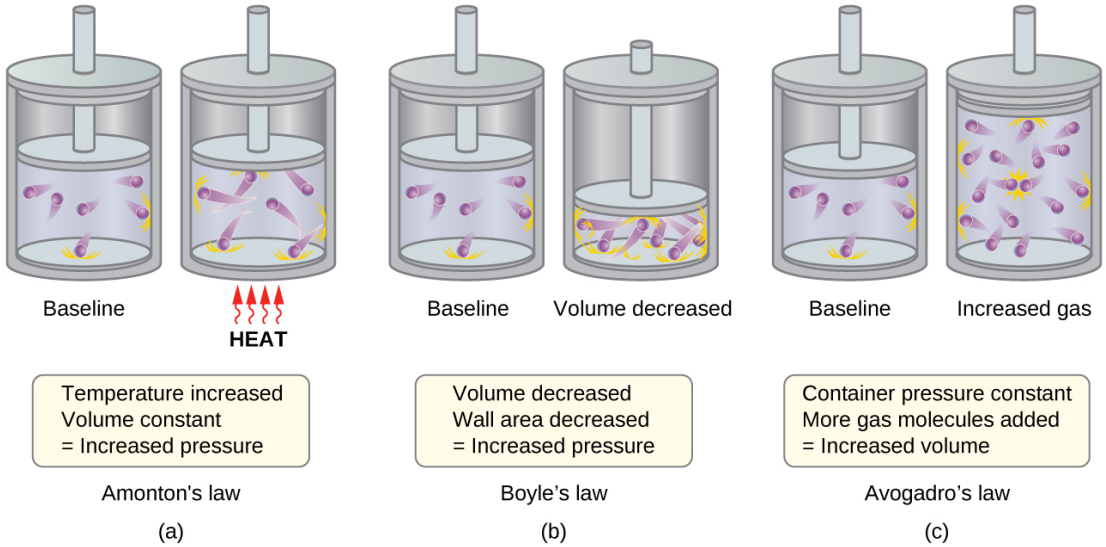


Figure **6.2.2.1**: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

6.2.2.2: molecular speeds and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at speeds and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure **6.2.2.2**).

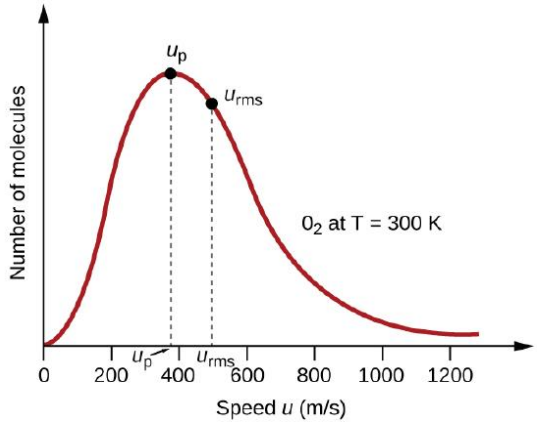


Figure **6.2.2.2**: The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$KE = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square speed of a particle, u_{rms}, is defined as the square root of the average of the squares of the speeds with n = the number of particles:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy for a mole of particles, KE_{avg}, is then equal to:

$$KE_{avg} = \frac{1}{2} M u_{rms}^2$$

where M is the molar mass expressed in units of kg/mol. The KE_{avg} of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$KE_{avg} = \frac{3}{2} RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/mol·K (8.314 kg $m^2 s^{-2} mol^{-1} K^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2} M u_{rms}^2 = \frac{3}{2} RT$$

with

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Example 6.2.2.1: Calculation of u_{rms}

Calculate the root-mean-square speed for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30^\circ C + 273 = 303 K$$

Determine the molar mass of nitrogen in kilograms:

Extra close brace or missing open brace

Replace the variables and constants in the root-mean-square speed equation, replacing Joules with the equivalent kg $m^2 s^{-2}$:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$u_{rms} = \sqrt{\frac{3(8.314 J/molK)(303K)}{(0.028 kg/mol)}} = \sqrt{2.70 \times 10^5 m^2 s^{-2}} = 519 m/s$$

Exercise 6.2.2.1

Calculate the root-mean-square speed for a mole of oxygen molecules at –23 °C.

Answer

441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more

molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in Figure **6.2.2.3**.

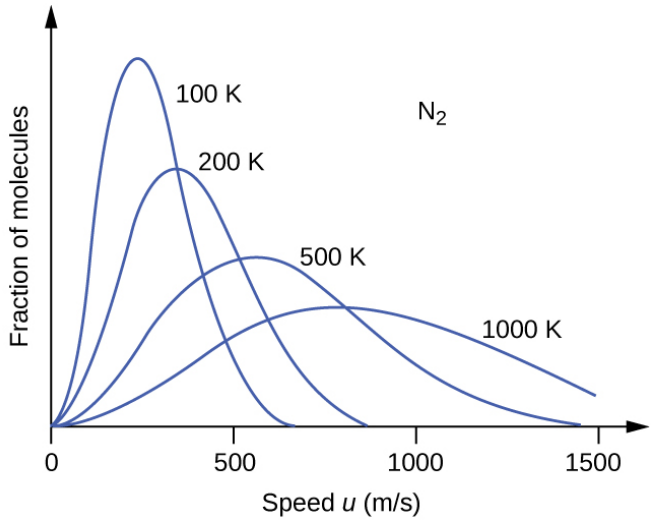


Figure **6.2.2.3**: The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher speeds. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower speeds. This trend is demonstrated by the data for a series of noble gases shown in Figure **6.2.2.4**.

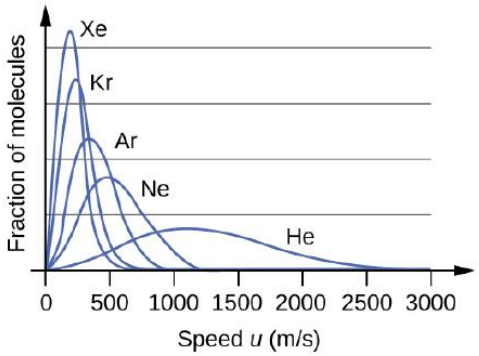


Figure **6.2.2.4**: molecular speed is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

Link to Learning

The gas simulator may be used to examine the effect of temperature on molecular speeds. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

6.2.2.3: The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate} \propto u_{rms}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$M = \frac{3RT}{u_{rms}^2} = \frac{3RT}{\bar{u}^2}$$

$$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \frac{u_{rmsA}}{u_{rmsB}} = \frac{\sqrt{\frac{3RT}{M_A}}}{\sqrt{\frac{3RT}{M_B}}} = \sqrt{\frac{M_B}{M_A}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

This page titled 6.2.2: The Kinetic-Molecular Theory is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **9.5: The Kinetic-Molecular Theory** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.3: Exercises

1.

Why are sharp knives more effective than dull knives? (Hint: Think about the definition of pressure.)

2.

Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?

3.

Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

4.

A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.

5.

A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

6.

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?

7.

Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

8.

During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?

9.

The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

10.

A medical laboratory catalog describes the pressure in a cylinder of a gas as 14.82 MPa. What is the pressure of this gas in atmospheres and torr?

11.

Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in. Hg, 1013.9 mbar.

(a) What was the pressure in kPa?

(b) The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.

12.

Why is it necessary to use a nonvolatile liquid in a barometer or manometer?

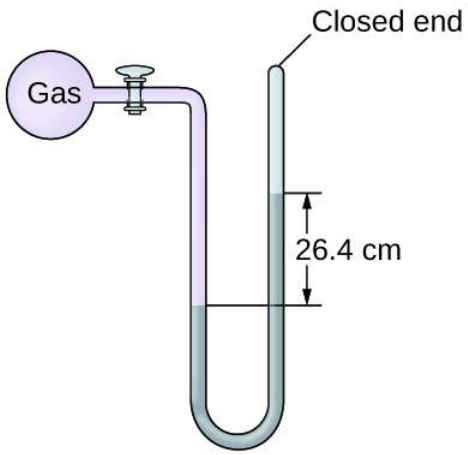
13.

The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

(a) torr

(b) Pa

(c) bar



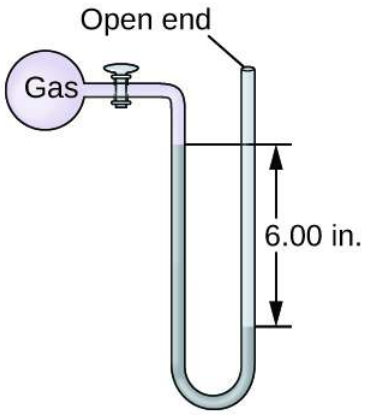
14.

The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 29.92 in. Hg, determine the pressure of the gas in:

(a) torr

(b) Pa

(c) bar



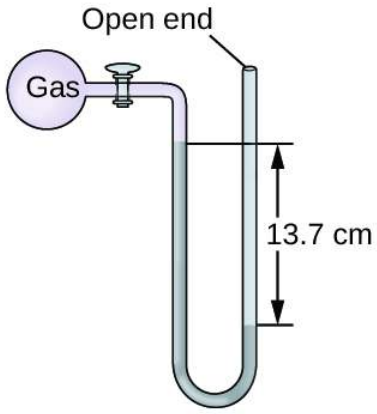
15.

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

(a) mm Hg

(b) atm

(c) kPa



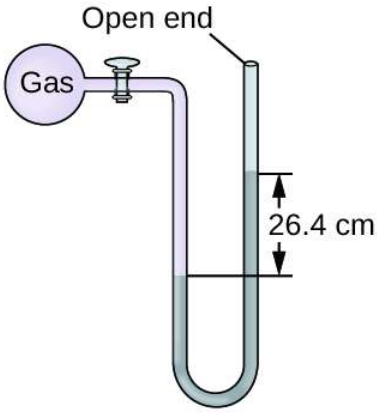
16.

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760 mm Hg, determine the pressure of the gas in:

(a) mm Hg

(b) atm

(c) kPa



17.

How would the use of a volatile liquid affect the measurement of a gas using open-ended manometers vs. closed-end manometers?

18.

Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

19.

Explain how the volume of the bubbles exhausted by a scuba diver (Figure 8.16) change as they rise to the surface, assuming that they remain intact.

20.

One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must be equal?

21.

An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas." (a) What is the meaning of the term "directly proportional?" (b) What are the "other things" that must be equal?

22.

How would the graph in Figure 8.12 change if the number of moles of gas in the sample used to determine the curve were doubled?

23.

How would the graph in Figure 8.13 change if the number of moles of gas in the sample used to determine the curve were doubled?

24.

In addition to the data found in Figure 8.13, what other information do we need to find the mass of the sample of air used to determine the graph?

25.

Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using Figure 8.12.

26.

Determine the pressure of the gas in the syringe shown in Figure 8.13 when its volume is 12.5 mL, using:

(a) the appropriate graph

(b) Boyle's law

27.

A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

28.

What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

29.

A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

30.

A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

31.

A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?



32.

The volume of an automobile air bag was 66.8 L when inflated at 25 °C with 77.8 g of nitrogen gas. What was the pressure in the bag in kPa?

33.

How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3?

34.

Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

35.

How many grams of gas are present in each of the following cases?

(a) 0.100 L of CO_2 at 307 torr and 26 °C

(b) 8.75 L of C_2H_4, at 378.3 kPa and 483 K

(c) 221 mL of Ar at 0.23 torr and –54 °C

36.

A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is 63.1 torr?

37.

A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

38.

A large scuba tank (Figure 8.16) with a volume of 18 L is rated for a pressure of 220 bar. The tank is filled at 20 °C and contains enough air to supply 1860 L of air to a diver at a pressure of 2.37 atm (a depth of 45 feet). Was the tank filled to capacity at 20 °C?

39.

A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

40.

While resting, the average 70-kg human male consumes 14 L of pure O_2 per hour at 25 °C and 100 kPa. How many moles of O_2 are consumed by a 70 kg man while resting for 1.0 h?

41.

For a given amount of gas showing ideal behavior, draw labeled graphs of:

(a) the variation of P with V

(b) the variation of V with T

(c) the variation of P with T

(d) the variation of $\frac{1}{P}$ with V

42.

A liter of methane gas, CH_4, at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.

43.

The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $CH_3CH_2F(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

(a) $CCl_2F_2(g)$

(b) $CH_3CH_2F(g)$

44.

As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

45.

A balloon with a volume of 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpit in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpit?

46.

If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

47.

If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

48.

What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?

49.

Calculate the density of Freon 12, CF_2Cl_2, at 30.0 °C and 0.954 atm.

50.

Which is denser at the same temperature and pressure, dry air or air saturated with water vapor? Explain.

51.

A cylinder of $O_2(g)$ used in breathing by patients with emphysema has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass of oxygen is in the cylinder?

52.

What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

53.

What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr?

54.

How could you show experimentally that the molecular formula of propene is C_3H_6, not CH_2?

55.

The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP. Calculate the molar mass of this fluoride and determine its molecular formula.

56.

Consider this question: What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies 125 mL with a pressure of 99.5 kPa at 22 °C?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

57.

A 36.0–L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO_2, 805 g O_2, and 4,880 g N_2. At 25 degrees C, what is the pressure in the cylinder in atmospheres?

58.

A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO_2, 12.0% O_2, and the remainder N_2 at a total pressure of 146 atm. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

59.

A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

60.

A mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar is stored in a closed container at STP. Find the volume of the container, assuming that the gases exhibit ideal behavior.

61.

Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O_2 is not. If enough O_2 is added to a cylinder of H_2 at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?

62.

A commercial mercury vapor analyzer can detect, in air, concentrations of gaseous Hg atoms (which are poisonous) as low as 2×10^{-6} mg/L of air. At this concentration, what is the partial pressure of gaseous mercury if the atmospheric pressure is 733 torr at 26 °C?

63.

A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18 °C. What is the pressure of the carbon monoxide? (See Table 8.2 for the vapor pressure of water.)

64.

In an experiment in a general chemistry laboratory, a student collected a sample of a gas over water. The volume of the gas was 265 mL at a pressure of 753 torr and a temperature of 27 °C. The mass of the gas was 0.472 g. What was the molar mass of the gas?

65.

Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:

$$2HgO\,(s) \longrightarrow 2Hg\,(l) + O_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of O_2 at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?

(b) Answer the question.

66.

Cavendish prepared hydrogen in 1766 by the novel method of passing steam through a red-hot gun barrel:

$$4H_2O\,(g) + 3Fe\,(s) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$

(a) Outline the steps necessary to answer the following question: What volume of H_2 at a pressure of 745 torr and a temperature of 20 °C can be prepared from the reaction of 15.O g of H_2O?

(b) Answer the question.

67.

The chlorofluorocarbon CCl_2F_2 can be recycled into a different compound by reaction with hydrogen to produce $CH_2F_2(g)$, a compound useful in chemical manufacturing:

$$CCl_2F_2(g) + 4H_2(g) \longrightarrow CH_2F_2(g) + 2HCl\,(g)$$

(a) Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of CCl_2F_2?

(b) Answer the question.

68.

Automobile air bags are inflated with nitrogen gas, which is formed by the decomposition of solid sodium azide (NaN_3). The other product is sodium metal. Calculate the volume of nitrogen gas at 27 °C and 756 torr formed by the decomposition of 125 g of sodium azide.

69.

Lime, CaO, is produced by heating calcium carbonate, $CaCO_3$; carbon dioxide is the other product.

(a) Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875 K and 0.966 atm is produced by the decomposition of 1 ton (1.000×10^3 kg) of calcium carbonate?

(b) Answer the question.

70.

Before small batteries were available, carbide lamps were used for bicycle lights. Acetylene gas, C_2H_2, and solid calcium hydroxide were formed by the reaction of calcium carbide, CaC_2, with water. The ignition of the acetylene gas provided the light. Currently, the same lamps are used by some cavers, and calcium carbide is used to produce acetylene for carbide cannons.

(a) Outline the steps necessary to answer the following question: What volume of C_2H_2 at 1.005 atm and 12.2 °C is formed by the reaction of 15.48 g of CaC_2 with water?

(b) Answer the question.

71.

Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of temperature and pressure.

72.

What volume of O_2 at STP is required to oxidize 8.0 L of NO at STP to NO_2? What volume of NO_2 is produced at STP?

73.

Consider the following questions:

(a) What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at 600 °C and 0.888 atm produced by the combustion of 1.00 L of $C_2H_6(g)$ measured at STP?

(b) What is the partial pressure of H_2O in the product gases?

74.

Methanol, CH_3OH, is produced industrially by the following reaction:

$$\mathrm{CO}\,(g) + 2\mathrm{H_2}(g) \xrightarrow{\text{copper catalyst 300 °C, 300 atm}} \mathrm{CH_3OH}\,(g)$$

Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

75.

What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of BaO_2 to BaO and O_2?

76.

A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of N_2 and 1.25 L of O_2 at STP. What is the colorless gas?

77.

Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

$$3\mathrm{C_2H_4} + 2\mathrm{H_2SO_4} \longrightarrow \mathrm{C_2H_5HSO_4} + (\mathrm{C_2H_5})_2\mathrm{SO_4}$$

$$\mathrm{C_2H_5HSO_4} + (\mathrm{C_2H_5})_2\mathrm{SO_4} + 3\mathrm{H_2O} \longrightarrow 3\mathrm{C_2H_5OH} + 2\mathrm{H_2SO_4}$$

What volume of ethylene at STP is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

78.

One molecule of hemoglobin will combine with four molecules of oxygen. If 1.0 g of hemoglobin combines with 1.53 mL of oxygen at body temperature (37 °C) and a pressure of 743 torr, what is the molar mass of hemoglobin?

79.

A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

80.

One method of analyzing amino acids is the van Slyke method. The characteristic amino groups ($-NH_2$) in protein material are allowed to react with nitrous acid, HNO_2, to form N_2 gas. From the volume of the gas, the amount of amino acid can be determined. A 0.0604-g sample of a biological sample containing glycine, $CH_2(NH_2)COOH$, was analyzed by the van Slyke method and yielded 3.70 mL of N_2 collected over water at a pressure of 735 torr and 29 °C. What was the percentage of glycine in the sample?

$$\mathbf{CH_2\,(NH_2)\,CO_2H + HNO_2 \longrightarrow CH_2\,(OH)\,CO_2H + H_2O + N_2}$$

81.

A balloon filled with helium gas takes 6 hours to deflate to 50% of its original volume. How long will it take for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50%?

82.

Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the center illustration of Figure 8.27.

83.

Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses.

84.

Heavy water, D_2O (molar mass = 20.03 g mol^{-1}), can be separated from ordinary water, H_2O (molar mass = 18.01), as a result of the difference in the relative rates of diffusion of the molecules in the gas phase. Calculate the relative rates of diffusion of H_2O and D_2O.

85.

Which of the following gases diffuse more slowly than oxygen? F_2, Ne, N_2O, C_2H_2, NO, Cl_2, H_2S

86.

During the discussion of gaseous diffusion for enriching uranium, it was claimed that $^{235}UF_6$ diffuses 0.4% faster than $^{238}UF_6$. Show the calculation that supports this value. The molar mass of $^{235}UF_6$ = 235.043930 + 6 × 18.998403 = 349.034348 g/mol, and the molar mass of $^{238}UF_6$ = 238.050788 + 6 × 18.998403 = 352.041206 g/mol.

87.

Calculate the relative rate of diffusion of $^1H_2$ (molar mass 2.0 g/mol) compared with $^2H_2$ (molar mass 4.0 g/mol) and the relative rate of diffusion of O_2 (molar mass 32 g/mol) compared with O_3 (molar mass 48 g/mol).

88.

A gas of unknown identity diffuses at a rate of 83.3 mL/s in a diffusion apparatus in which carbon dioxide diffuses at the rate of 102 mL/s. Calculate the molecular mass of the unknown gas.

89.

When two cotton plugs, one moistened with ammonia and the other with hydrochloric acid, are simultaneously inserted into opposite ends of a glass tube that is 87.0 cm long, a white ring of NH_4Cl forms where gaseous NH_3 and gaseous HCl first come into contact. $\mathbf{NH_3}(g) + \mathbf{HCl}(g) \longrightarrow \mathbf{NH_4Cl}(s)$ At approximately what distance from the ammonia moistened plug does this occur? (Hint: Calculate the rates of diffusion for both NH_3 and HCl, and find out how much faster NH_3 diffuses than HCl.)

90.

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

91.

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

92.

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

(a) The pressure of the gas is increased by reducing the volume at constant temperature.

(b) The pressure of the gas is increased by increasing the temperature at constant volume.

(c) The average speed of the molecules is increased by a factor of 2.

93.

The distribution of molecular speeds in a sample of helium is shown in Figure 8.34. If the sample is cooled, will the distribution of speeds look more like that of H_2 or of H_2O? Explain your answer.

94.

What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms}, of the two gases?

95.

A 1-L sample of CO initially at STP is heated to 546 K, and its volume is increased to 2 L.

(a) What effect do these changes have on the pressure exerted by the gas?

(b) What is the effect on the average kinetic energy of the molecules?

(c) What is the effect on the root mean square speed of the molecules?

96.

The root mean square speed of H_2 molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N_2 molecule at 25 °C?

97.

Answer the following questions:

(a) Is the pressure of the gas in the hot-air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

(b) Is the density of the gas in the hot-air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

(c) At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?

(d) The average temperature of the gas in a hot-air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.

(e) The lifting capacity of a hot-air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?

(f) An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft^3. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?

(g) A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane at STP?

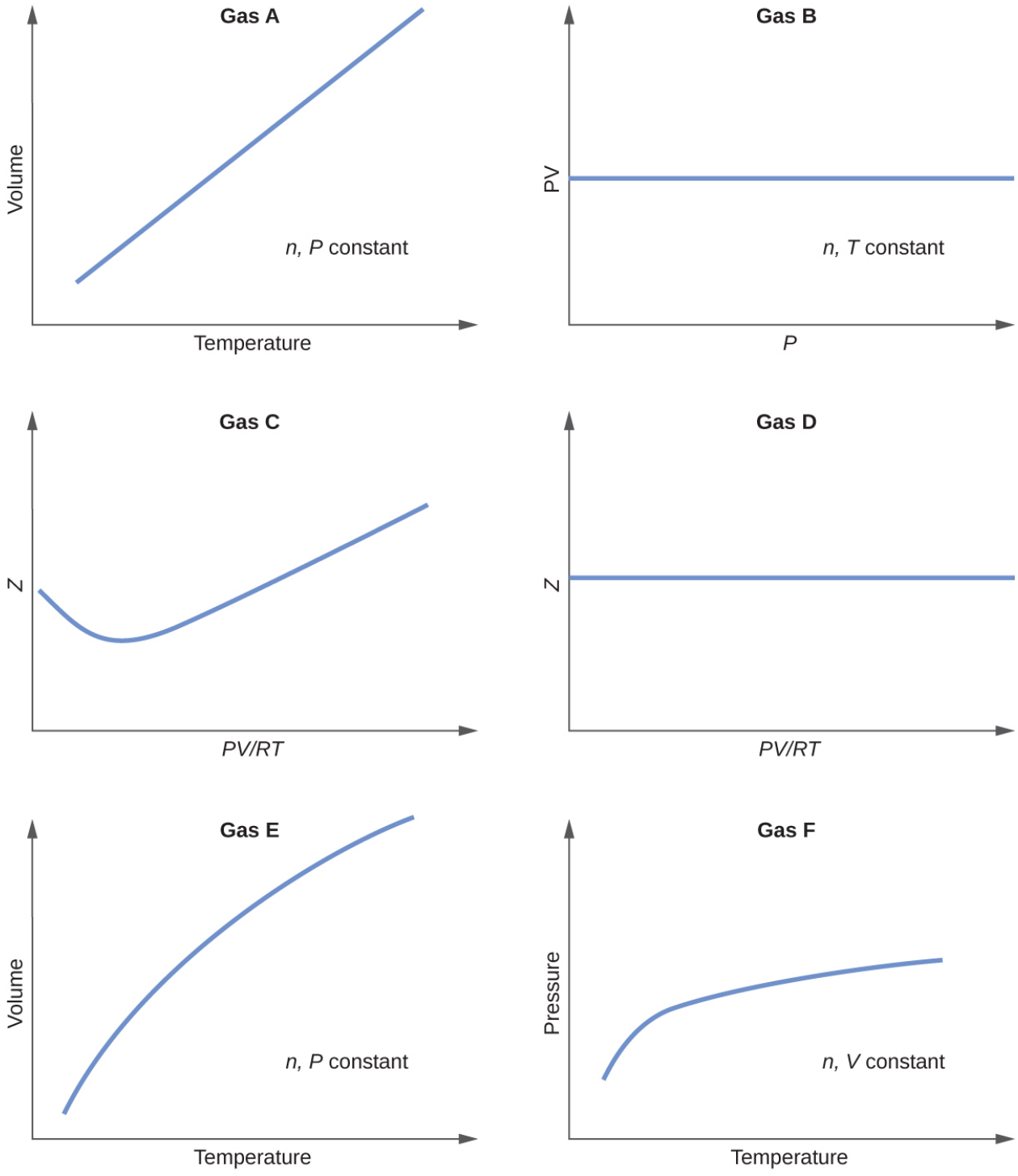
(h) A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?

98.

Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $\frac{R_1}{R_2}$, is the same at 0 °C and 100 °C.

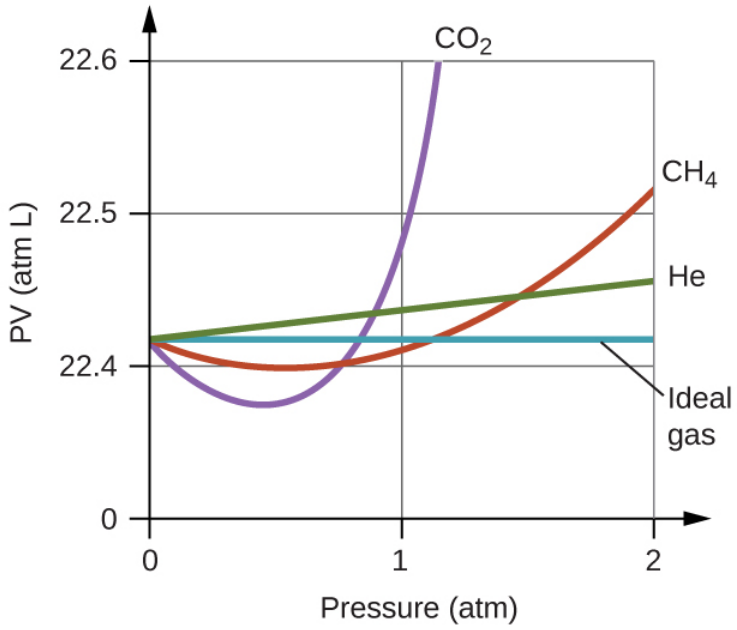
99.

Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?



100.

Explain why the plot of PV for CO_2 differs from that of an ideal gas.



101.

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

(a) high pressure, small volume

(b) high temperature, low pressure

(c) low temperature, high pressure

102.

Describe the factors responsible for the deviation of the behavior of real gases from that of an

ideal gas.

103.

For which of the following gases should the correction for the molecular volume be largest:

CO, CO_2, H_2, He, NH_3, SF_6?

104.

A 0.245-L flask contains 0.467 mol CO_2 at 159 °C. Calculate the pressure:

(a) using the ideal gas law

(b) using the van der Waals equation

(c) Explain the reason for the difference.

(d) Identify which correction (that for P or V) is dominant and why.

105.

Answer the following questions:

(a) If XX behaved as an ideal gas, what would its graph of Z vs. P look like?

(b) For most of this chapter, we performed calculations treating gases as ideal. Was this justified?

(c) What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

(d) What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

(e) In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

This page titled 6.3: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

6.3.1: Answers to Selected Exercises

1.

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

3.

Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

5.

0.809 atm; 82.0 kPa

7.

2.2×10^2 kPa

9.

Earth: 14.7 lb in^{-2}; Venus: 1.30×10^3 lb in^{-2}

11.

(a) 101.5 kPa; (b) 51 torr drop

13.

(a) 264 torr; (b) 35,200 Pa; (c) 0.352 bar

15.

(a) 623 mm Hg; (b) 0.820 atm; (c) 83.1 kPa

17.

With a closed-end manometer, no change would be observed, since the vaporized liquid would contribute equal, opposing pressures in both arms of the manometer tube. However, with an open-ended manometer, a higher pressure reading of the gas would be obtained than expected, since $P_{gas} = P_{atm} + P_{vol\ liquid}$.

19.

As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

21.

(a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure

23.

The curve would be farther to the right and higher up, but the same basic shape.

25.

About 12.5 L

27.

3.40×10^3 torr

29.

12.1 L

31.

217 L

33.

8.190×10^{-2} mol; 5.553 g

35.

(a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g

37.

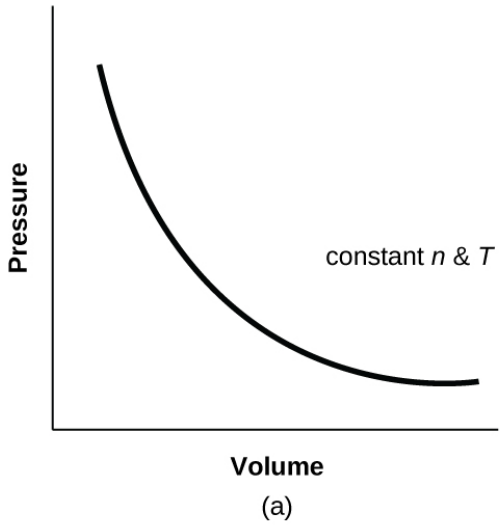
5561 L

39.

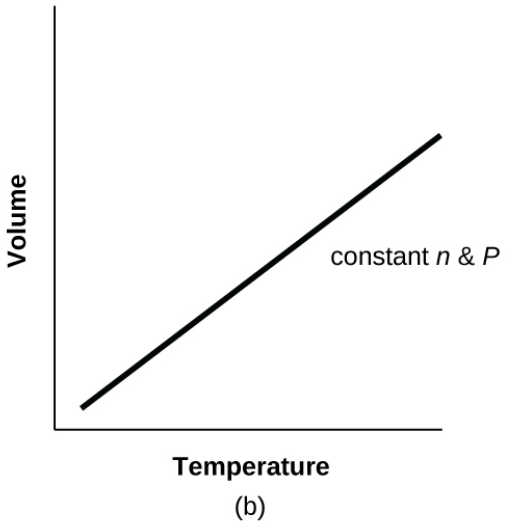
46.4 g

41.

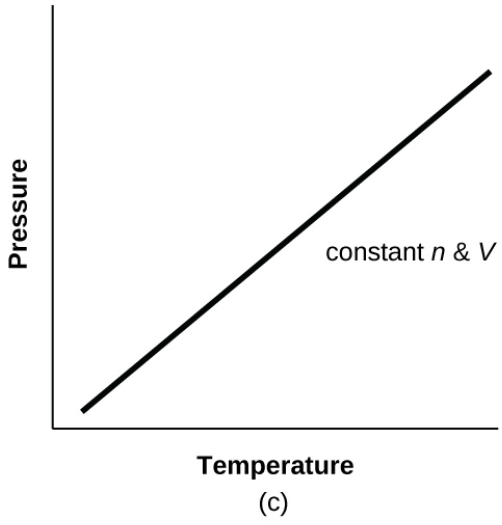
For a gas exhibiting ideal behavior:



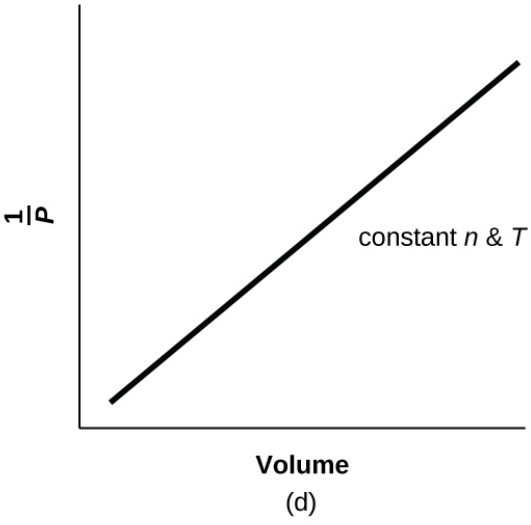
(a)



(b)



(c)



(d)

43.

(a) 1.85 L CCl_2F_2; (b) 4.66 L CH_3CH_2F

45.

0.644 atm

47.

The pressure decreases by a factor of 3.

49.

4.64 g L^{-1}

51.

38.8 g

53.

72.0 g mol^{-1}

55.

88.1 g mol^{-1}; PF_3

57.

141 atm

59.

CH_4: 276 kPa; C_2H_6: 27 kPa; C_3H_8: 3.4 kPa

61.

Yes

63.

740 torr

65.

(a) Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO; and determine the volume of O_2 from the moles of O_2, temperature, and pressure. (b) 0.308 L

67.

(a) Determine the molar mass of CCl_2F_2. From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2 into volume. (b) 3.72×10^3 L

69.

(a) Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas. (b) 7.43×10^5 L

71.

42.00 L

73.

(a) 18.0 L; (b) 0.533 atm

75.

10.57 L O_2

77.

5.40×10^5 L

79.

XeF_4

81.

4.2 hours

83.

Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $(\text{mfrac}) = (\text{mfrac})^{1/2}$. Both A and B are in the same container at the same temperature, and therefore

will have the same kinetic energy:

$\mathbf{KE_A = KE_B KE =}$

Therefore, $\frac{1}{2}m_A v_A^2 =$

$\frac{v_A^2}{v_B^2} =$

$\left(\frac{v_A^2}{v_B^2}\right)^{1/2} = \left(\frac{m_B}{m_A}\right)^{1/2}$

$\frac{v_A}{v_B} = \left(\frac{m_B}{m_A}\right)^{1/2}$

85.

F_2, N_2O, Cl_2, H_2S

87.

1.4; 1.2

89.

51.7 cm

91.

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average speed of all the molecules is constant at constant temperature.

93.

H_2O. Cooling slows the speeds of the He atoms, causing them to behave as though they were heavier.

95.

(a) The pressure of the gas remains constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\sqrt{\mathbf{KE_{avg}}}$.

97.

(a) equal; (b) less than; (c) 29.48 g mol^{-1}; (d) 1.0966 g L^{-1}; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}

99.

Gases C, E, and F

101.

The gas behavior most like an ideal gas will occur under the conditions that minimize the chances of significant interactions between the gaseous atoms/molecules, namely, low pressures (fewer atoms/molecules per unit volume) and high temperatures (greater kinetic energies of atoms/molecules make them less susceptible to attractive forces). The conditions described in (b), high temperature and low pressure, are therefore most likely to yield ideal gas behavior.

103.

SF_6

105.

(a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures, they behave close enough to ideal gases that they are approximated as such; however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation. (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure 8.35). (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See Figure 8.35. (e) Low temperatures

This page titled 6.3.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

7: Chemical Reactions and Stoichiometry

7.1: Writing and Balancing Chemical Equations
7.2: Classifying Chemical Reactions
7.3: Reaction Stoichiometry
7.4: Reaction Yields
7.5: Exercises
7.5.1: Answers to Selected Exercises

This page titled 7: Chemical Reactions and Stoichiometry is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

7.1: Writing and Balancing Chemical Equations

Learning Objectives

By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

An earlier chapter of this text introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure **7.1.1**: , with space-filling molecular models shown in the lower half of the figure.

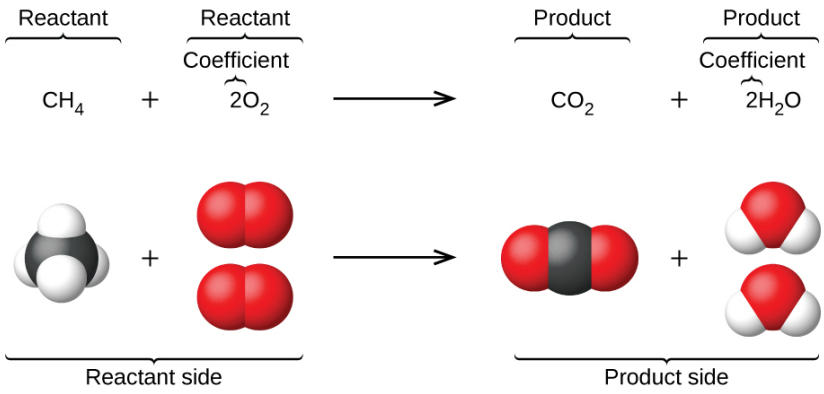


Figure **7.1.1**: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called reactants, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called products, and their formulas are placed on the right side of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by coefficients (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure **7.1.2**). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

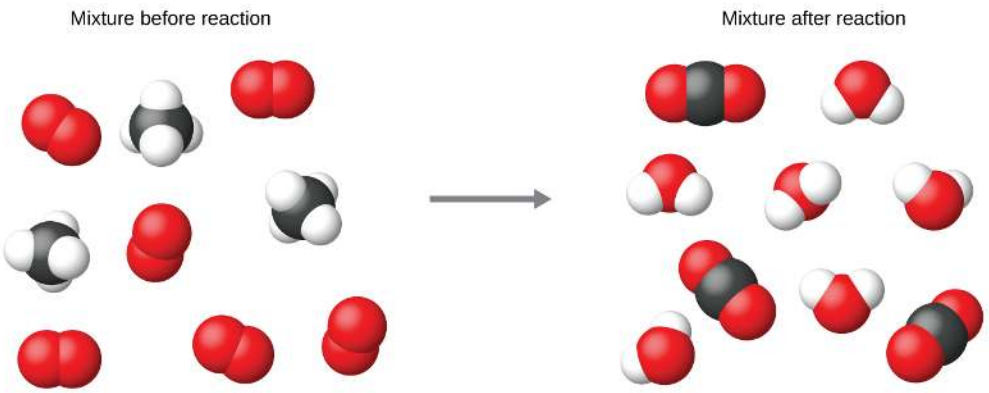


Figure **7.1.2**: Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

7.1.1: Balancing Equations

The chemical equation described above in Figure **7.1.1** is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1CO_2 \text{ molecule} \times \frac{2O \text{ atoms}}{CO_2 \text{ molecule}}\right) + \left(2H_2O \text{ molecules} \times \frac{1O \text{ atom}}{H_2O \text{ molecule}}\right) = 4O \text{ atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$\mathrm{H_2O \longrightarrow H_2 + O_2} \qquad \textbf{(unbalanced)}$$

Comparing the number of **H** and **O** atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$\mathbf{2\,H_2O \longrightarrow H_2 + O_2} \qquad \textbf{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$\mathbf{2\,H_2O \longrightarrow 2\,H_2 + O_2} \qquad \textbf{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 4	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$\mathbf{H_2O \longrightarrow H_2 + O_2} \qquad \textbf{(balanced)}$$

Example 7.1.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$\mathbf{N_2 + O_2 \longrightarrow N_2O_5} \qquad \textbf{(unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 2 = 2	1 2 = 2	2 = 2, yes
O	1 2 = 2	1 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$\mathbf{N_2 + 5\,O_2 \longrightarrow 2\,N_2O_5} \qquad \textbf{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2\,N_2 + 5\,O_2 \longrightarrow 2\,N_2O_5 \qquad \text{(balanced)}$$

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

? Exercise 7.1.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$$2\,NH_4NO_3 \longrightarrow 2\,N_2 = O_2 + 4\,H_2O$$

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \longrightarrow H_2O + CO_2 \qquad \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \longrightarrow 3\,H_2O + 2\,CO_2 \qquad \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \tfrac{7}{2}\,O_2 \longrightarrow 3\,H_2O + 2\,CO_2 \qquad \text{(unbalanced)}$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 6\,H_2O + 4\,CO_2 \qquad \text{(balanced)}$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3\,N_2 + 9\,H_2 \longrightarrow 6\,NH_3$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

Link to Learning

Use this interactive tutorial for additional practice balancing equations.

7.1.2: Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in

water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\,Na\,(s) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2\,(g)$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + CO_2\,(g)$$

Other examples of these special conditions will be encountered in more depth in later chapters.

7.1.3: Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid AgCl:

$$CaCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Ca(NO_3)_2\,(aq) + 2\,AgCl\,(s)$$

This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$CaCl_2\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2\,Cl^-\,(aq)$$
$$2\,AgNO_3\,(aq) \longrightarrow 2\,Ag^+\,(aq) + 2\,NO_3^-\,(aq)$$
$$Ca(NO_3)_2\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2\,NO_3^-\,(aq)$$

Unlike these three ionic compounds, **AgCl** does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) + 2\,Ag^+\,(aq) + 2\,NO_3^-\,(aq) \longrightarrow Ca^{2+}\,(aq) + 2\,NO_3^-\,(aq) + 2\,AgCl\,(s)$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

$$\cancel{Ca^{2+}\,(aq)} + 2\,Cl^-\,(aq) + 2\,Ag^+\,(aq) + \cancel{2NO3^-\,(aq)} \longrightarrow \cancel{Ca^{2+}\,(aq)} + \cancel{2NO3^-\,(aq)} + 2\,AgCl\,(s)$$
$$2\,Cl^-\,(aq) + 2\,Ag^+\,(aq) \longrightarrow 2\,AgCl\,(s)$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$Cl^-\,(aq) + Ag^+\,(aq) \longrightarrow AgCl\,(s)$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

Example 7.1.2: Ionic and Molecular Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$\mathrm{CO_2\,(aq) + NaOH\,(aq) \longrightarrow Na_2CO_3\,(aq) + H_2O\,(l)} \qquad \text{(unbalanced)}$$

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$\mathrm{CO_2\,(aq) + 2\,NaOH\,(aq) \longrightarrow Na_2CO_3\,(aq) + H_2O\,(l)}$$

The two dissolved ionic compounds, NaOH and $\mathrm{Na_2CO_3}$, can be represented as dissociated ions to yield the complete ionic equation:

$$\mathrm{CO_2\,(aq) + 2\,Na^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,Na^+\,(aq) + CO_3^{2-}\,(aq) + H_2O\,(l)}$$

Finally, identify the spectator ion(s), in this case $\mathrm{Na^+}(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$\mathrm{CO_2\,(aq) + \cancel{2Na^+\,(aq)} + OH^-\,(aq) \longrightarrow \cancel{2Na^+\,(aq)} + CO_3^{2-}\,(aq) + H_2O\,(l)}$$

$$\mathrm{CO_2\,(aq) + OH^-\,(aq) \longrightarrow CO_3^{2-}\,(aq) + H_2O\,(l)}$$

Exercise 7.1.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$\mathrm{NaCl\,(aq) + H_2O\,(l) \xrightarrow{electricity} NaOH\,(aq) + H_2\,(g) + Cl_2\,(g)}$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

$$\mathrm{2\,NaCl\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,NaOH\,(aq) + H_2\,(g) + Cl_2\,(g)} \qquad \text{(molecular)}$$

$$\mathrm{2\,Na^+\,(aq) + 2\,Cl^-\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,Na^+\,(aq) + 2\,OH^-\,(aq) + H_2\,(g) + Cl_2\,(g)} \qquad \text{(complete ionic)}$$

$$\mathrm{2\,Cl^-\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,OH^-\,(aq) + H_2\,(g) + Cl_2\,(g)} \qquad \text{(net ionic)}$$

This page titled 7.1: Writing and Balancing Chemical Equations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **4.1: Writing and Balancing Chemical Equations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.2: Classifying Chemical Reactions

Learning Objectives

By the end of this section, you will be able to:

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

7.2.1: 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 a later 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 **7.2.1**).

Table 7.2.1

	contain these ions	exceptions
Soluble Ionic Compounds	NH_4^+ group I cations: Li^+ Na^+ K^+ Rb^+ Cs^+	none
	Cl^- Br^- I^-	compounds with Ag^+, Hg_2^{2+}, and Pb^{2+}
	F^-	compounds with group 2 metal cations, Pb^{2+}, and Fe^{3+}
	$C_2H_3O_2^-$ HCO_3^- NO_3^- ClO_3^-	none
	SO_4^{2-}	compounds with Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+} and Sr^{2+}
Insoluble Ionic Compounds	contain these ions	exceptions
	CO_3^{2-} CrO_4^{2-} PO_4^{3-} S^{2-}	compounds with group 1 cations and NH_4^+
	OH^-	compounds with group 1 cations and Ba^{2+}

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:

$$\mathbf{2\,KI\,(aq) + Pb(NO_3)_2\,(aq) \longrightarrow PbI_2\,(s) + 2\,KNO_3\,(aq)}$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$\mathbf{Pb^{2+}\,(aq) + 2\,I^{-}\,(aq) \longrightarrow PbI_2\,(s)}$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 7.2.1). The properties of pure $\mathbf{PbI_2}$ crystals make them useful for fabrication of X-ray and gamma ray detectors.

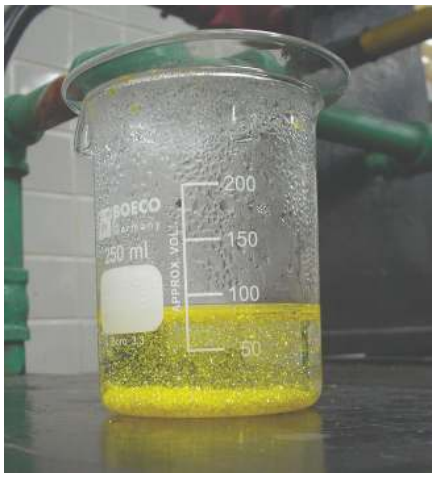


Figure 7.2.1: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table 7.2.1 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 one of insoluble. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$\mathrm{NaCl\,(aq) + AgNO_3\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)} \quad \text{(molecular)}$$

$$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)} \quad \text{(net ionic)}$$

Example 7.2.1: Predicting Precipitation Reactions

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

$$\mathrm{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)}$$

(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

$$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)}$$

(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

$$\mathrm{Pb^{2+}\,(aq) + CO_3{}^{2-}\,(aq) \longrightarrow PbCO_3\,(s)}$$

? Exercise 7.2.1

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, $\mathbf{BaSO_4}$

7.2.2: 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:

$$\mathbf{HCl\,(aq) + H_2O\,(aq) \longrightarrow Cl^-\,(aq) + H_3O^+\,(aq)}$$

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 **7.2.2**).

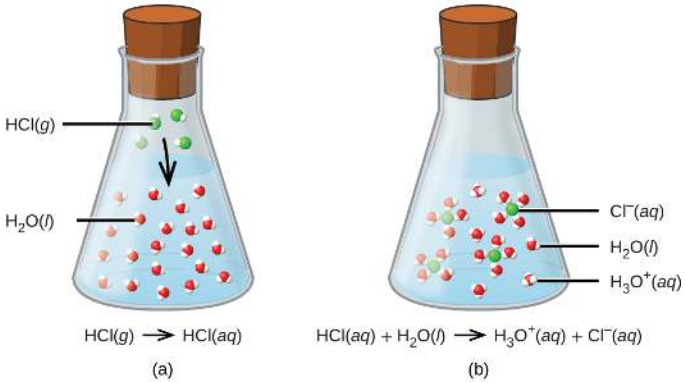
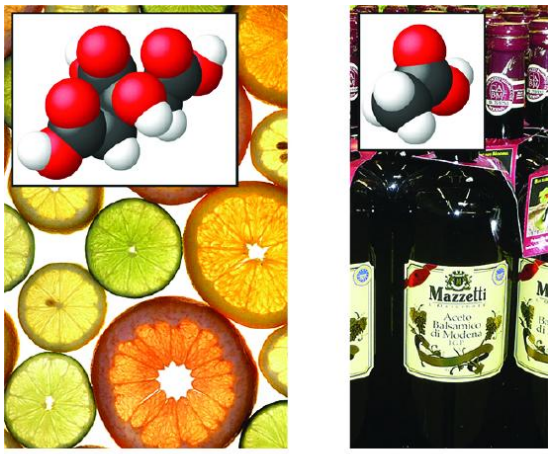


Figure **7.2.2**: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

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 **7.2.2**). 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:

$$\mathbf{CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2^-\,(aq) + H_3O^+\,(aq)}$$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form,



(a) (b)

Figure **7.2.3**: (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 **7.2.2**: 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 $Ca(OH)_2$. Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions 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:

$$\mathrm{NaOH\,(s) \longrightarrow Na^+\,(aq) + OH^-\,(aq)}$$

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 **7.2.4**). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)}$$

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 ions.



Figure **7.2.4**: 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)

A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a salt and water

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

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):

$$Mg(OH)_2\,(s) + 2\,HCl\,(aq) \longrightarrow MgCl_2\,(aq) + 2\,H_2O\,(l)$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

✔ Example 7.2.2: 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^-.

$$HOCl\,(aq) + H_2O\,(l) \rightleftharpoons OCl^-\,(aq) + H_3O^+\,(aq)$$

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

$$Ba(OH)_2\,(aq) + 2\,HNO_3\,(aq) \longrightarrow Ba(NO_3)_2\,(aq) + 2\,H_2O\,(l)$$

? Exercise 7.2.2

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

$$H_3O^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,H_2O\,(l)$$

Chemistry in Everyday Life: Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$\mathrm{CaCO_3\,(s) + 2\,HCl\,(aq) \rightleftharpoons CaCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)}$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$\mathrm{Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

$$\mathrm{H_3O^+ + OH^- \rightleftharpoons 2\,H_2O\,(l)}$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Chemistry in Everyday Life: Culinary Aspects of Chemistry

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure **7.2.5**). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.



$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Putrescine}}{NH_2CH_2CH_2CH_2CH_2NH_2} \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{Putrescinium ion}}{NH_3^+CH_2CH_2CH_2CH_2NH_2}$$

Figure **7.2.5**: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

Link to Learning

Explore the microscopic view of strong and weak acids and bases.

7.2.3: Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\,Na\,(s) + Cl_2\,(g) \longrightarrow 2\,NaCl\,(s)$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2\,Na\,(s) \longrightarrow 2\,Na^+\,(s) + 2\,e^-$$
$$Cl_2\,(g) + 2\,e^- \longrightarrow 2\,Cl^-\,(s)$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\text{oxidation} = \text{loss of electrons}$$
$$\text{reduction} = \text{gain of electrons}$$

In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent** (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent** (oxidant), as it effectively removes electrons from (oxidizes) sodium.

$$\text{reducing agent} = \text{species that is oxidized}$$
$$\text{oxidizing agent} = \text{species that is reduced}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound were ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
   - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
   - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, very rarely (so-called superoxides, positive values when combined with F (values vary)
   - Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

✔ Example 7.2.3: Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. $\mathrm{H_2S}$
b. $\mathrm{SO_3^{2-}}$
c. $\mathrm{Na_2SO_4}$

Solution

(a) According to guideline 3, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$
$$x = 0 - (2 \times +1) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } {SO_3}^{2-} = -2 = (3 \times -2) + (1 \times x)$$
$$x = -2 - (3 \times -2) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on } SO_4^{2-} = -2 = (4 \times -2) + (1 \times x)$$
$$x = -2 - (4 \times -2) = +6$$

? Exercise 7.2.3

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

a. $\mathrm{K\underline{N}O_3}$
b. $\mathrm{\underline{Al}H_3}$
c. $\mathrm{\underline{N}H_4^+}$
d. $\mathrm{H_2\underline{P}O_4^-}$

Answer

a. N, +5;
b. Al, +3;
c. N, −3;
d. P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist Example 4.6.) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\text{oxidation} = \text{increase in oxidation number}$$
$$\text{reduction} = \text{decrease in oxidation number}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$\text{oxidation} = \text{increase in oxidation number}$$
$$\text{reduction} = \text{decrease in oxidation number}$$

Link to Learning

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\mathrm{Cu\,(s) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,Ag\,(s)}$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure **7.2.6**).

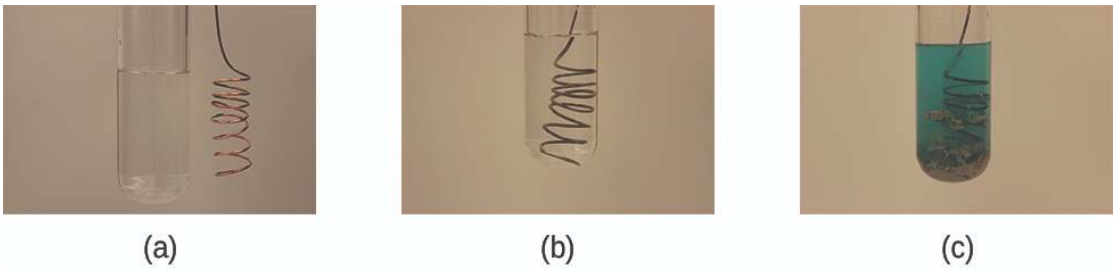


Figure **7.2.6**: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 7.2.4: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $\mathrm{ZnCO_3\,(s) \longrightarrow ZnO\ (s) + CO_2\,(g)}$
b. $\mathrm{2\,Ga\,(l) + 3\,Br_2\,(l) \longrightarrow 2\,GaBr_3\,(s)}$
c. $\mathrm{2\,H_2O_2\,(aq) \longrightarrow 2\,H_2O\,(l) + O_2\,(g)}$
d. $\mathrm{BaCl_2\,(aq) + K_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2\,KCl\,(aq)}$
e. $\mathrm{C_2H_4\,(g) + 3\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)}$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in $GaBr_3$(s). The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(l) to −1 in $GaBr_3$(s). The oxidizing agent is Br_2(l).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in H_2O_2(aq) to 0 in O_2(g). Oxygen is also reduced, its oxidation number decreasing from −1 in H_2O_2(aq) to −2 in H_2O(l). For disproportionation reactions, the same substance functions as an oxidant and a reductant.
d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C_2H_4(g) to +4 in CO_2(g). The reducing agent (fuel) is C_2H_4(g). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(g) to −2 in H_2O(l). The oxidizing agent is O_2(g).

Exercise 7.2.4

This equation describes the production of tin(II) chloride:

$$\mathrm{Sn\,(s) + 2\,HCl\,(g) \longrightarrow SnCl_2\,(s) + H_2\,(g)}$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. $\mathrm{Sn(s)}$ is the reductant and $\mathrm{HCl(g)}$ is the oxidant.

7.2.4: Footnotes

- 1The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

This page titled 7.2: Classifying Chemical Reactions is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **4.2: Classifying Chemical Reactions** is licensed CC BY 4.0.

7.3: Reaction Stoichiometry

Learning Objectives

By the end of this section, you will be able to:

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Food preparation, for example, offers an appropriate comparison. A recipe for making eight pancakes calls for 1 cup pancake mix, cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \longrightarrow 8 \text{ pancakes}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \cancel{\text{ pancakes}} \times \frac{1 \text{ egg}}{8 \cancel{\text{ pancakes}}} = 3 \text{ eggs}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)}$$

This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2 \text{ NH}_3 \text{ molecules}}{3 \text{ H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 7.3.1: Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure **7.3.1**)?

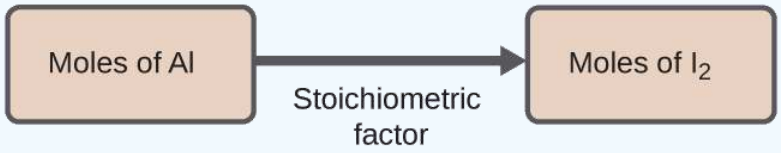
$$\mathrm{2\,Al + 3\,I_2 \longrightarrow 2\,AlI_3}$$



Figure 7.3.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$mol\,I_2 = 0.429\,\text{mol Al} \times \frac{3\,\text{mol}\,I_2}{2\,\text{mol Al}}$$
$$= 0.644\,\text{mol}\,I_2$$

Exercise 7.3.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation

Answer

2.04 mol

Example 7.3.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

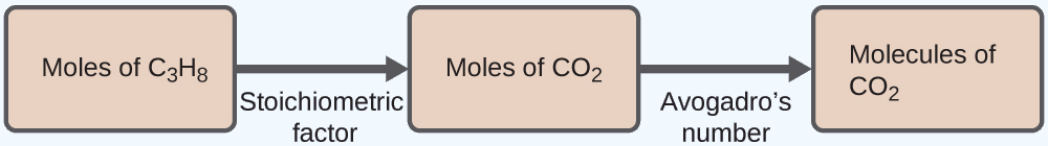
Solution

The approach here is the same as for Example 7.3.1, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3\,\text{mol}\,CO_2}{1\,\text{mol}\,C_3H_8}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75mol\,{}_3CH_8 \times \frac{3molCO_2}{1mol\,C_3H_8} \times \frac{6.022 \times 10^{23}\,CO_2\ \text{molecules}}{mol\,CO_2} = 1.4 \times 10^{24}\,CO_2\ \text{molecules}$$

Exercise 7.3.2

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O$$

Answer

4.8 10^{24} NH_3 molecules

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

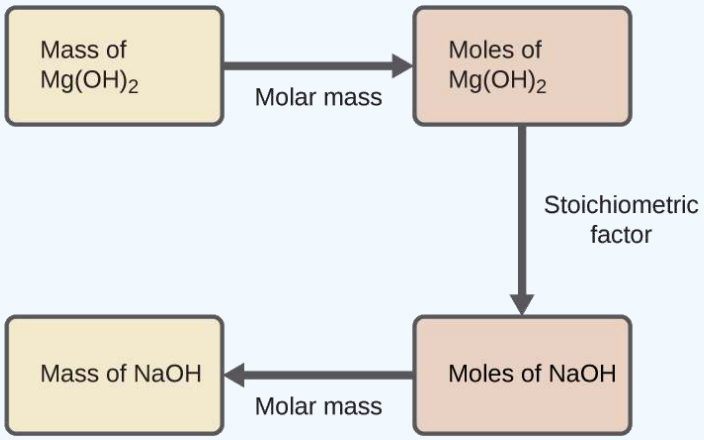
Example 7.3.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2\,(aq) + 2\,NaOH\,(aq) \longrightarrow Mg(OH)_2\,(s) + 2\,NaCl\,(aq)$$

Solution

The approach used previously in Example 7.3.1 and Example 7.3.2 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16g\,Mg(OH)_2 \times \frac{1mol\,Mg(OH)_2}{58.3g\,Mg(OH)_2} \times \frac{2\,mol\,NaOH}{1\,mol\,Mg(OH)_2} \times \frac{40.0\,g\,NaOH}{mol\,NaOH} = 22\,g\,NaOH$$

Exercise 7.3.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is:

$$4\,Ga + 3\,O_2 \longrightarrow 2\,Ga_2O_3$$

Answer

39.0 g

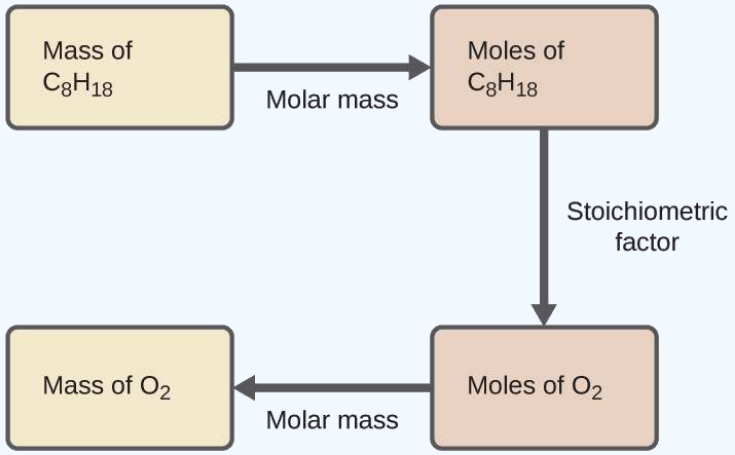
Example 7.3.4: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$\mathbf{2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O}$$

Solution

The approach required here is the same as for the Example **7.3.3**, differing only in that the provided and requested masses are both for reactant species.



$$702 g C_8H_{18} \times \frac{1 mol C_8H_{18}}{114.23 g G_8H_{18}} \times \frac{25 mol O_2}{2 mol C_8H_{18}} \times \frac{32.00 g O_2}{mol O_2} = 2.46 \times 10^3 g O_2$$

Exercise 7.3.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\mathbf{Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2}$?

Answer

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure **7.3.2**: provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

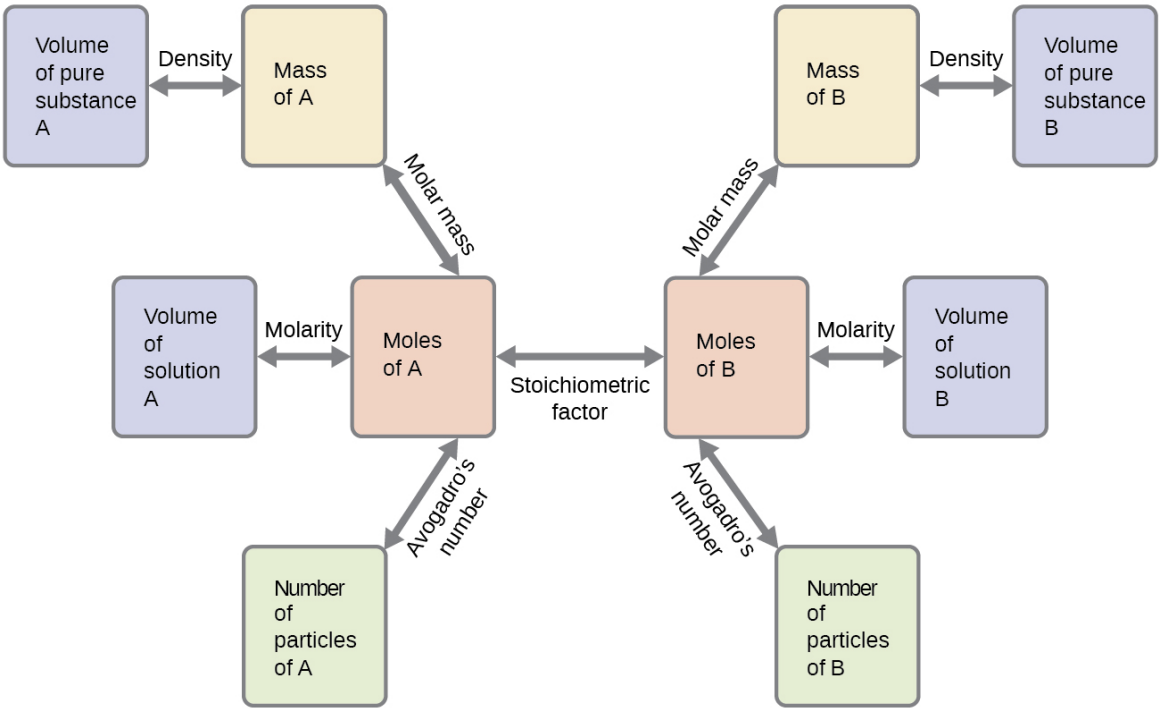


Figure **7.3.2**: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Chemistry in Everyday Life: Airbags

Airbags (Figure **7.3.3**) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$\mathbf{2\,NaN_3\,(s) \longrightarrow 3\,N_2\,(g) + 2\,Na\,(s)}$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure **7.3.3**: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

This page titled 7.3: Reaction Stoichiometry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **4.3: Reaction Stoichiometry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.4: Reaction Yields

Learning Objectives

By the end of this section, you will be able to:

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

7.4.1: Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure **7.4.1**):

$$\text{1 slice of cheese} + \text{2 slices of bread} \longrightarrow \text{1 sandwich}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

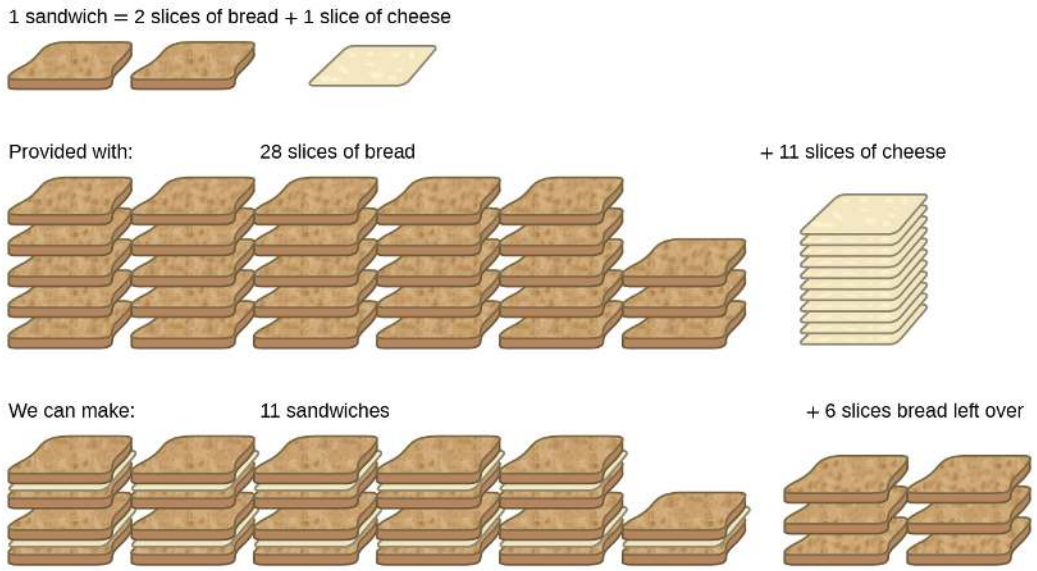


Figure **7.4.1**: Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g)}$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the **limiting reactant**, and the other substance(s) is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric

ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 3\,\text{mol H}_2 \times \frac{2\,\text{mol HCl}}{1\,\text{mol H}_2} = 6\,\text{mol HCl}$$

Complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\,\text{mol Cl}_2 \times \frac{2\,\text{mol HCl}}{1\,\text{mol Cl}_2} = 4\,\text{mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure **7.4.2**).

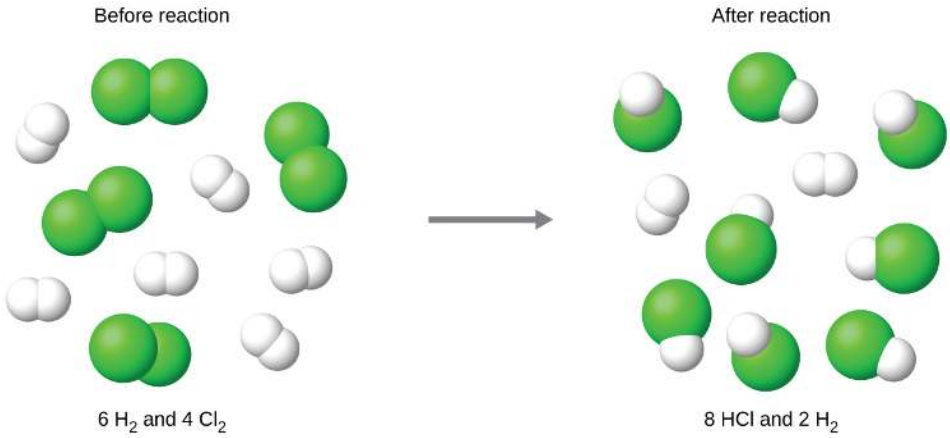


Figure **7.4.2**: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

Link to Learning

View this interactive simulation illustrating the concepts of limiting and excess reactants.

Example 7.4.1: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3Si(s) + 2N_2(g) \longrightarrow Si_3N_4(s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$molSi = 2.00gSi \times \frac{1molSi}{28.09gSi} = 0.0712molSi$$

$$molSi = 2.00gSi \times \frac{1molSi}{28.09gSi} = 0.0712molSi$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712 mol Si}{0.0535 mol N_2} = \frac{1.33 mol Si}{1 mol N_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3 mol Si}{2 mol N_2} = \frac{1.5 mol Si}{1 mol N_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$mol Si_3N_4 \text{ produced } = 0.0712 mol Si \times \frac{1 mol Si_3N_4}{3 mol Si^2} = 0.0237 mol Si_3N_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol Si } N_4 \text{ produced } = 0.0535 mol N \times \frac{1 mol Si_3N_4}{2 mol N_2} = 0.0268 mol Si_3N_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

? Exercise 7.4.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer

O_2

7.4.2: Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this chapter). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

$$\text{percent yield } = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{7.4.1}$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

✔ Example 7.4.2: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$CuSO_4(aq) + Zn(s) \longrightarrow Cu(s) + ZnSO_4(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$$1.274\,\text{g}\,\text{CuSO}_4 \times \frac{1\,\text{mol}\,\text{CuSO}_4}{159.62\,\text{g}\,\text{CuSO}_4} \times \frac{1\,\text{mol}\,\text{Cu}}{1\,\text{mol}\,\text{CuSO}_4} \times \frac{63.55\,\text{g}\,\text{Cu}}{1\,\text{mol}\,\text{Cu}} = 0.5072\,\text{g}\,\text{Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated (via Equation 7.4.1 to be

$$\begin{aligned}\text{percent yield} &= \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100\% \\ &= \left(\frac{0.392\,\text{g}\,\text{Cu}}{0.5072\,\text{g}\,\text{Cu}_2}\right) \times 100\% \\ &= 77.3\%\end{aligned}$$

Exercise 7.4.2

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$CCl_4 + 2\,HF \longrightarrow CF_2Cl_2 + 2\,HCl$$

Answer

48.3%

How Sciences Interconnect: Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry" (see details at this website). One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

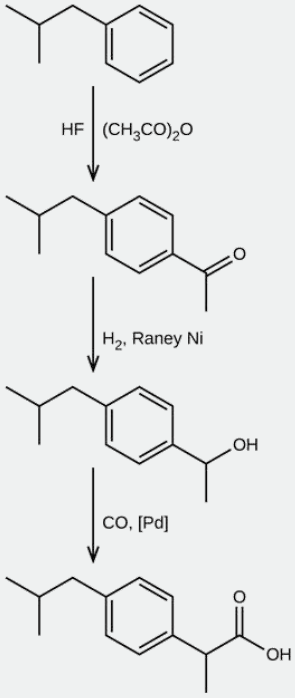
$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure **7.4.3**). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.



(a)



(b)

Figure **7.4.3**: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

This page titled 7.4: Reaction Yields is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **4.4: Reaction Yields** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.5: Exercises

Writing and Balancing Chemical Equations

1. What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

2. Consider molecular, complete ionic, and net ionic equations.

   (a) What is the difference between these types of equations?
   (b) In what circumstance would the complete and net ionic equations for a reaction be identical?

3. Balance the following equations:

   (a) $PCl_5(s) + H_2O(l) \longrightarrow POCl_3(l) + HCl(aq)$
   (b) $Cu(s) + HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l) + NO(g)$
   (c) $H_2(g) + I_2(s) \longrightarrow HI(s)$
   (d) $Fe(s) + O_2(g) \longrightarrow Fe_2O_3(s)$
   (e) $Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$
   (f) $(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + N_2(g) + H_2O(g)$
   (g) $P_4(s) + Cl_2(g) \longrightarrow PCl_3(l)$
   (h) $PtCl_4(s) \longrightarrow Pt(s) + Cl_2(g)$

4. Balance the following equations

   (a) $Ag(s) + H_2S(g) + O_2(g) \longrightarrow Ag_2S(s) + H_2O(l)$
   (b) $P_4(s) + O_2(g) \longrightarrow P_4O_{10}(s)$
   (c) $Pb(s) + H_2O(l) + O_2(g) \longrightarrow Pb(OH)_2(s)$
   (d) $Fe(s) + H_2O(l) \longrightarrow Fe_3O_4(s) + H_2(g)$
   (e) $Sc_2O_3(s) + SO_3(l) \longrightarrow Sc_2(SO_4)_3(s)$
   (f) $Ca_3(PO_4)_2(aq) + H_3PO_4(aq) \longrightarrow Ca(H_2PO_4)_2(aq)$
   (g) $Al(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(s) + H_2(g)$
   (h) $TiCl_4(s) + H_2O(g) \longrightarrow TiO_2(s) + HCl(g)$

5. Write a balanced molecular equation describing each of the following chemical reactions.

   (a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
   (b) Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.
   (c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
   (d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

6. Write a balanced equation describing each of the following chemical reactions.

   (a) Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.
   (b) Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.
   (c) When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.
   (d) Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

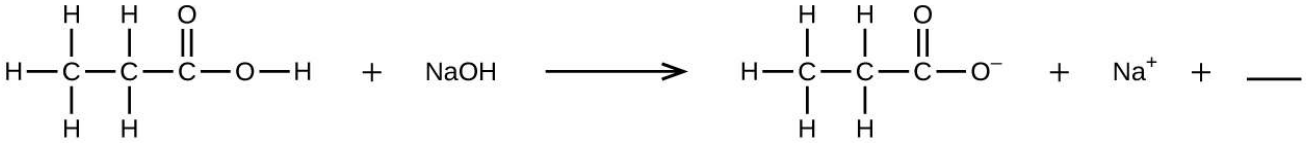
7. Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

   (a) Write the formulas of barium nitrate and potassium chlorate.
   (b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
   (c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and

diatomic oxygen gas. Write an equation for the reaction.

(d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

8. Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



9. Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

a. Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.

b. The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

10. A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

a. The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

b. The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

c. Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

d. The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

e. Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

11. From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

(a) $K_2C_2O_4(aq) + Ba(OH)_2(aq) \longrightarrow 2KOH(aq) + BaC_2O_4(s)$

(b) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$

(c) $CaCO_3(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

7.2 Classifying Chemical Reactions

12. Use the following equations to answer the next four questions:

i. $H_2O(s) \longrightarrow H_2O(l)$

ii. $Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

iii. $CH_3OH(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

iv. $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

v. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

(a) Which equation describes a physical change?

(b) Which equation identifies the reactants and products of a combustion reaction?

(c) Which equation is not balanced?

(d) Which is a net ionic equation?

13. Indicate what type, or types, of reaction each of the following represents:

(a) $Ca(s) + Br_2(l) \longrightarrow CaBr_2(s)$
(b) $Ca(OH)_2(aq) + 2HBr(aq) \longrightarrow CaBr_2(aq) + 2H_2O(l)$
(c) $C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$

14. Indicate what type, or types, of reaction each of the following represents:

(a) $H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$
(b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$
(c) $Al(OH)_3(aq) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(l)$
(d) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$

15. Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction? Explain your answer.

16. Determine the oxidation states of the elements in the following compounds:

(a) NaI
(b) $GdCl_3$
(c) $LiNO_3$
(d) H_2Se
(e) Mg_2Si
(f) RbO_2, rubidium superoxide
(g) HF

17. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_3PO_4
(b) $Al(OH)_3$
(c) SeO_2
(d) KNO_2
(e) In_2S_3
(f) P_4O_6

18. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_2SO_4
(b) $Ca(OH)_2$
(c) BrOH
(d) $ClNO_2$
(e) $TiCl_4$
(f) NaH

19. Classify the following as acid-base reactions or oxidation-reduction reactions:

(a) $Na_2S(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2S(g)$
(b) $2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$
(c) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
(d) $MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$
(e) $K_3P(s) + 2O_2(g) \longrightarrow K_3PO_4(s)$
(f) $3KOH(aq) + H_3PO_4(aq) \longrightarrow K_3PO_4(aq) + 3H_2O(l)$

20. Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

(a) $Mg(s) + NiCl_2(aq) \longrightarrow MgCl_2(aq) + Ni(s)$
(b) $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$
(d) $Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$
(e) $2\ K_2\ S_2O_3(s) + I_2(s) \longrightarrow K_2\ S_4O_6(s) + 2KI(s)$
(f) $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu\,(NO_3)_2\,(aq) + 2NO(g) + 4H_2O(l)$

21. Complete and balance the following acid-base equations:

a. HCl gas reacts with solid $Ca(OH)_2(s)$.
b. A solution of $Sr(OH)_2$ is added to a solution of HNO_3.

22. Complete and balance the following acid-base equations:

a. A solution of $HClO_4$ is added to a solution of LiOH.
b. Aqueous H_2SO_4 reacts with NaOH.
c. $Ba(OH)_2$ reacts with HF gas.

23. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

(a) $Al(s) + F_2(g)$
(b) $Al(s) + CuBr_2(aq)$
$\longrightarrow$ (single displacement)
(c) $P_4(s) + O_2(g)$
(d) $Ca(s) + H_2O(l) \longrightarrow$ (products are a strong base and a diatomic gas)

24. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

(a) $K(s) + H_2O(l) \rightarrow$
(b) $Ba(s) + HBr(aq) \rightarrow$
(c) $Sn(s) + I_2(s) \rightarrow$

25. Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.

(a) $Mg(OH)_2(s) + HClO_4(aq)$
(b) $SO_3(g) + H_2O(l)$ (assume an excess of water and that the product dissolves)
(c) $SrO(s) + H_2SO_4(l)$

26. When heated to $700 - 800°C$, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.

27. The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

28. Write the molecular, total ionic, and net ionic equations for the following reactions:

(a) $Ca(OH)_2(aq) + HC_2H_3O_2(aq)$
(b) $H_3PO_4(aq) + CaCl_2(aq)$

29. Great Lakes Chemical Company produces bromine, Br_2, from bromide salts such as NaBr , in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of NaBr with Cl_2.23. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

30. In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce MgO. MgO is a white solid, but in these experiments it often looks gray, due to small amounts of Mg_3N_2, a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.

31.Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)

32. Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.

33. Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:

(a) $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2\ S}(g)$
(b) $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2\ S}(g) \longrightarrow$

34. Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid dihydrogen sulfate as the only product. Write the two equations which represent these reactions.

35. Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.

a. solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)
b. gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction
c. gaseous H_2S from solid Zn and S via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)

36. Calcium cyclamate $Ca(C_6H_{11}NHSO_3)_2$ is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid $C_6H_{11}NHSO_3H$ with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.

37. Complete and balance each of the following half-reactions (steps $\mathbf{2-5}$ in half-reaction method):

(a) $\mathrm{Sn^{4+}}(aq) \longrightarrow \mathrm{Sn^{2+}}(aq)$
(b) $\mathrm{[Ag\,(NH_3)_2]^+}\,(aq) \longrightarrow \mathrm{Ag}(s) + \mathrm{NH_3}(aq)$
(c) $\mathrm{Hg_2Cl_2}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{Cl^-}(aq)$
(d) $\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g)$ (in acidic solution)
(e) $\mathrm{IO_3^-}(aq) \longrightarrow \mathrm{I_2}(s)$ (in basic solution)
(f) $\mathrm{SO_3^{2-}}(aq) \longrightarrow \mathrm{SO_4^{2-}}(aq)$ (in acidic solution)
(g) $\mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)$ (in acidic solution)
(h) $\mathrm{Cl^-}(aq) \longrightarrow \mathrm{ClO_3^-}(aq)$ (in basic solution)

38. Complete and balance each of the following half-reactions (steps $\mathbf{2-5}$ in half-reaction method):

(a) $\mathrm{Cr^{2+}}(aq) \longrightarrow \mathrm{Cr^{3+}}(aq)$
(b) $\mathrm{Hg}(l) + \mathrm{Br^-}(aq) \longrightarrow \mathrm{HgBr_4^{2-}}(aq)$
(c) $\mathrm{ZnS}(s) \longrightarrow \mathrm{Zn}(s) + \mathrm{S^{2-}}(aq)$
(d) $\mathrm{H_2}(g) \longrightarrow \mathrm{H_2O}(l)$ (in basic solution)
(e) $\mathrm{H_2}(g) \longrightarrow \mathrm{H_3O^+}(aq)$ (in acidic solution)
(f) $\mathrm{NO_3^-}(aq) \longrightarrow \mathrm{HNO_2}(aq)$ (in acidic solution)
(g) $\mathrm{MnO_2}(s) \longrightarrow \mathrm{MnO_4^-}(aq)$ (in basic solution)
(h) $\mathrm{Cl^-}(aq) \longrightarrow \mathrm{ClO_3^-}(aq)$ (in acidic solution)

39. Balance each of the following equations according to the half-reaction method:

(a) $\mathrm{Sn^{2+}}(aq) + \mathrm{Cu^{2+}}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq) + \mathrm{Cu^+}(aq)$
(b) $\mathrm{H_2\ S}(g) + \mathrm{Hg_2^{2+}}(aq) \longrightarrow \mathrm{Hg}(l) + \mathrm{S}(s)$ (in acid)
(c) $\mathrm{CN^-}(aq) + \mathrm{ClO_2}(aq) \longrightarrow \mathrm{CNO^-}(aq) + \mathrm{Cl^-}(aq)$ (in acid)

(d) $Fe^{2+}(aq) + Ce^{4+}(aq) \longrightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$

(e) $HBrO(aq) \longrightarrow Br^{-}(aq) + O_2(g)$ (in acid)

Reaction Stoichiometry

42. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

(a) The number of moles and the mass of chlorine, Cl_2, required to react with 10.0 g of sodium metal, Na , to produce sodium chloride, NaCl .

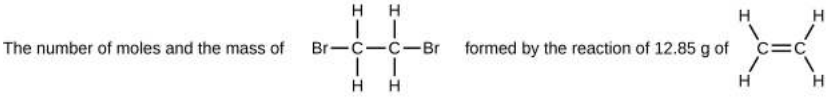
(b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.

(c) The number of moles and the mass of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)

(d) The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.

(e) The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)

The number of moles and the mass of



with an excess of Br_2.

43. Determine the number of moles and the mass requested for each reaction in Exercise 42.

44. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

(a) The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce $MgCl_2$ and H_2.

(b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver(l) oxide.

(c) The number of moles and the mass of magnesium carbonate, $MgCO_3$, required to produce 283 g of carbon dioxide. (MgO is the other product.)

(d) The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene, C_2H_2, in an excess of oxygen.

(e) The number of moles and the mass of barium peroxide, BaO_2, needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)

(f)



45. Determine the number of moles and the mass requested for each reaction in Exercise 4.44.

46. H_2 is produced by the reaction of 118.5 mL of a 0.8775-M solution of H_3PO_4 according to the following equation:

a. Outline the steps necessary to determine the number of moles and mass of H_2.

b. Perform the calculations outlined.

47. Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation:

a. Outline the steps necessary to determine the number of moles and mass of gallium chloride.

b. Perform the calculations outlined.

48. I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation:

a. How many molecules of I_2 are produced?

b. What mass of I_2 is produced?

49. Silver is often extracted from ores such as $K[Ag(CN)_2]$ and then recovered by the reaction

a. How many molecules of $Zn(CN)_2$ are produced by the reaction of 35.27 g of $K[Ag(CN)_2]$?
b. What mass of $Zn(CN)_2$ is produced?

50. What mass of silver oxide, Ag_2O, is required to produce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

51. Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much SiO_2 is required to produce 3.00 kg of SiC.

52. Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

What mass of sodium azide is required to produce 2.6 ft^3 (73.6 L) of nitrogen gas with a density of 1.25 g/L?

53. Urea, $CO(NH_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of of carbon followed by the reaction?

54. In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

55. A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

56. What volume of 0.750 M hydrochloric acid solution can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with excess sulfuric acid?

57. What volume of a 0.2089 *M* KI solution contains enough KI to react exactly with the $Cu(NO_3)_2$ in 43.88 mL of a 0.3842 *M* solution of $Cu(NO_3)_2$?

58. A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

What mass of $Ca(OH)_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

59. The toxic pigment called white lead, $Pb_3(OH)_2(CO_3)_2$, has been replaced in white paints by rutile, TiO_2. How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ($FeTiO_3$) by mass?

Reaction Yields

60. The following quantities are placed in a container: 1.5 10^{24} atoms of hydrogen, 1.0 mol of sulfur, and 88.0 g of diatomic oxygen.

a. What is the total mass in grams for the collection of all three elements?
b. What is the total number of moles of atoms for the three elements?
c. If the mixture of the three elements formed a compound with molecules that contain two hydrogen atoms, one sulfur atom, and four oxygen atoms, which substance is consumed first?
d. How many atoms of each remaining element would remain unreacted in the change described in (c)?

61. What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

62. Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?

63. A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

64. A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

65. Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

66. Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is

What mass of citric acid is produced from exactly 1 metric ton ($1.000\ 10^3$ kg) of sucrose if the yield is 92.30%?

67. Toluene, $C_6H_5CH_3$, is oxidized by air under carefully controlled conditions to benzoic acid, $C_6H_5CO_2H$, which is used to prepare the food preservative sodium benzoate, $C_6H_5CO_2Na$. What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid?

68. In a laboratory experiment, the reaction of 3.0 mol of H_2 with 2.0 mol of I_2 produced 1.0 mol of HI. Determine the theoretical yield in grams and the percent yield for this reaction.

69. Outline the steps needed to solve the following problem, then do the calculations. Ether, $(C_2H_5)_2O$, which was originally used as an anesthetic but has been replaced by safer and more effective medications, is prepared by the reaction of ethanol with sulfuric acid.

$$2C_2H_5OH + H_2SO_4 \longrightarrow (C_2H_5)_2O + H_2SO_4{\cdot}H_2O$$

What is the percent yield of ether if 1.17 L (d = 0.7134 g/mL) is isolated from the reaction of 1.500 L of C_2H_5OH (d = 0.7894 g/mL)?

70. Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen. Determine the limiting reactant.

71. Outline the steps needed to determine the limiting reactant when 0.50 mol of Cr and 0.75 mol of H_3PO_4 react according to the following chemical equation.

Determine the limiting reactant.

72. What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?

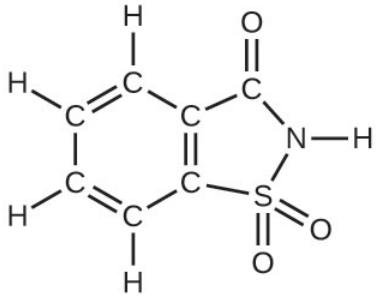
73. Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4){\cdot}3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_3)_2$, yields 1.073 g of solid $UO_2(C_2O_4){\cdot}3H_2O$.

$$Na_2C_2O_4 + UO_2(NO_3)_2 + 3H_2O \longrightarrow UO_2(C_2O_4){\cdot}3H_2O + 2NaNO_3$$

Determine the limiting reactant and the percent yield of this reaction.

74. How many molecules of $C_2H_4Cl_2$ can be prepared from 15 C_2H_4 molecules and 8 Cl_2 molecules?

75. How many molecules of the sweetener saccharin can be prepared from 30 C atoms, 25 H atoms, 12 O atoms, 8 S atoms, and 14 N atoms?



76. The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.

a. What is the limiting reactant when 0.200 mol of P_4 and 0.200 mol of O_2 react according to
b. Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

77. Would you agree to buy 1 trillion (1,000,000,000,000) gold atoms for $5? Explain why or why not. Find the current price of gold at http://money.cnn.com/data/commodities/

78. What volume of 0.0105-M HBr solution is required to titrate 125 mL of a 0.0100-*M* $Ca(OH)_2$ solution?

79. Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

80. What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 *M* $AgNO_3$ requires 20.22 mL of the $AgNO_3$ solution to reach the end point?

81. In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of 8.25 10^{-4} *M* $Hg(NO_3)_2(aq)$ to reach the end point?

82. Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCI to reach the end point?

83. A sample of gallium bromide, $GaBr_3$, weighing 0.165 g was dissolved in water and treated with silver nitrate, $AgNO_3$, resulting in the precipitation of 0.299 g AgBr. Use these data to compute the %Ga (by mass) $GaBr_3$.

84. The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of CO_2. Determine its empirical and molecular formulas.

85. A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of B_2O_3. What are the empirical and molecular formulas of the compound?

86. Sodium bicarbonate (baking soda), $NaHCO_3$, can be purified by dissolving it in hot water (60 °C), filtering to remove insoluble impurities, cooling to 0 °C to precipitate solid $NaHCO_3$, and then filtering to remove the solid, leaving soluble impurities in solution. Any $NaHCO_3$ that remains in solution is not recovered. The solubility of $NaHCO_3$ in hot water of 60 °C is 164 g/L. Its solubility in cold water of 0 °C is 69 g/L. What is the percent yield of $NaHCO_3$ when it is purified by this method?

87. What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

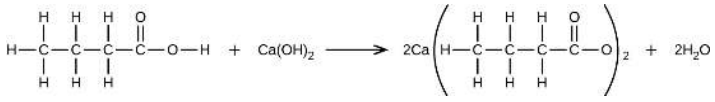
88. What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

89. What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

90. What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H_2SO_4 concentration of 1.23 10^{-4} *M*.

91. A sample of solid calcium hydroxide, $Ca(OH)_2$, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00 10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point. What is the molarity?

92. What mass of $Ca(OH)_2$ will react with 25.0 g of butanoic to form the preservative calcium butanoate according to the equation?



93. How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of H_3PO_4?

94. Potassium hydrogen phthalate, $KHC_8H_4O_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $KHC_8H_4O_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

95. The reaction of WCl_6 with Al at ~400 °C gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 *M* NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

This page titled 7.5: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **4.9: Exercises** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

7.5.1: Answers to Selected Exercises

1.

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

3.

(a) $PCl_5(s) + H_2O(l) \longrightarrow POCl_3(l) + 2HCl(aq)$; (b) $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$; (c) $H_2(g) + I_2(s) \longrightarrow 2HI(s)$; (d) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$; (e) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$; (f) $(NH_4msubmsub Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$; (g) $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(l)$; (h) $PtCl_4(s) \longrightarrow Pt(s) + 2Cl_2(g)$

5.

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$; (b) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$; (c) $MgCl_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaCl(aq)$; (d) $2H_2O(g) + 2Na(s) \longrightarrow 2NaOH(s) + H_2(g)$

7.

(a) $Ba(NO_3)_2$, $KClO_3$; (b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$; (c) $2Ba(NO_3)_2(s) \longrightarrow 2BaO(s) + 2N_2(g) + 5O_2(g)$; (d) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$; $4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$; $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$

9.

(a) $4HF(aq) + SiO_2(s) \longrightarrow SiF_4(g) + 2H_2O(l)$; (b) complete ionic equation: $2Na^+(aq) + 2F^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \longrightarrow CaF_2(s) + 2Na^+(aq) + 2Cl^-(aq)$, net ionic equation: $2F^-(aq) + Ca^{2+}(aq) \longrightarrow CaF_2(s)$

11.

(a) $2K^+(aq) + C_2O_4{}^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow 2K^+(aq) + 2OH^-(aq) + BaC_2O_4(s)$ (complete)
$Ba^{2+}(aq) + C_2O_4{}^{2-}(aq) \longrightarrow BaC_2O_4(s)$ (net)

(b) $Pb^{2+}(aq) + 2NO_3{}^-(aq) + 2H^+(aq) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s) + 2H^+(aq) + 2NO_3{}^-(aq)$ (complete)
$Pb^{2+}(aq) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s)$ (net)

(c) $CaCO_3(s) + 2H^+(aq) + SO_4{}^{2-}(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$ (complete)
$CaCO_3(s) + 2H^+(aq) + SO_4{}^{2-}(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$ (net)

13.

(a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

15.

It is an oxidation-reduction reaction because the oxidation state of the silver changes during the reaction.

17.

(a) H +1, P +5, O −2; (b) Al +3, H +1, O −2; (c) Se +4, O −2; (d) K +1, N +3, O −2; (e) In +3, S −2; (f) P +3, O −2

19.

(a) acid-base; (b) oxidation-reduction: Na is oxidized, H^+ is reduced; (c) oxidation-reduction: Mg is oxidized, Cl_2 is reduced; (d) acid-base; (e) oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; (f) acid-base

21.

(a) $2HCl(g) + Ca(OH)_2(s) \longrightarrow CaCl_2(s) + 2H_2O(l)$; (b) $Sr(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Sr(NO_3)_2(aq) + 2H_2O(l)$

23.

(a) $2Al(s) + 3F_2(g) \longrightarrow 2AlF_3(s)$; (b) $2Al(s) + 3CuBr_2(aq) \longrightarrow 3Cu(s) + 2AlBr_3(aq)$; (c) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$; (d) $Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$

25.

(a) $Mg(OH)_2(s) + 2HClO_4(aq) \longrightarrow Mg^{2+}(aq) + 2ClO_4{}^-(aq) + 2H_2O(l)$; (b) $SO_3(g) + 2H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4{}^-(aq)$, (a solution of H_2SO_4); (c) $SrO(s) + H_2SO_4(l) \longrightarrow SrSO_4(s) + H_2O$

27.

$H_2(g) + F_2(g) \longrightarrow 2HF(g)$

29.

$2NaBr(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + Br_2(l)$

31.

$2LiOH(aq) + CO_2(g) \longrightarrow Li_2CO_3(aq) + H_2O(l)$

33.

(a) $Ca(OH)_2(s) + H_2S(g) \longrightarrow CaS(s) + 2H_2O(l)$; (b) $Na_2CO_3(aq) + H_2S(g) \longrightarrow Na_2S(aq) + CO_2(g) + H_2O(l)$

35.

(a) step 1: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, step 2: $NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq) \longrightarrow NH_4NO_3(s)$ (after drying); (b) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$; (c) $Zn(s) + S(s) \longrightarrow ZnS(s)$ and $ZnS(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$

37.

(a) msup$(aq) + 2e^- \longrightarrow Sn^2$msup$(aq)$, (b) $[Ag(NH_3)_2]^+(aq) + e^- \longrightarrow Ag(s) + 2NH_3(aq)$; (c) $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2$msupmsup$(aq)$; (d) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$; (e) $6H_2O(l) + 2IO_3^-(aq) + 10$msupmsup $\longrightarrow I_2(s) + 12$msupmsup$(aq)$; (f) $H_2O(l) + SO_3^2$msup$(aq) \longrightarrow SO_4^2$msup$(aq) + 2H^+(aq) + 2e^-$; (g) $8H^+(aq) + MnO_4^-(aq) + 5e^- \longrightarrow Mn^2$msup$(aq) + 4H_2O(l)$; (h) $Cl^-(aq) + 6$msupmsup$(aq) \longrightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$

39.

(a) $Sn^{2+}(aq) + 2Cu^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2Cu^+(aq)$; (b) $H_2S(g) + Hg_2^{2+}(aq) + 2H_2O(l) \longrightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$; (c) $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \longrightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$; (d) $Fe^{2+}(aq) + Ce^{4+}(aq) \longrightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$; (e) $2HBrO(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + 2Br^-(aq) + O_2(g)$

41.

(a) $2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$; (b) $3MnO_4^{2-}(aq) + 2H_2O(l) \longrightarrow 2MnO_4^-(aq) + 4OH^-(aq) + MnO_2(s)$ (in base); (c) $Br_2(l) + SO_2(g) + 2H_2O(l) \longrightarrow 4H^+(aq) + 2Br^-(aq) + SO_4^{2-}(aq)$

43.

(a) 0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2; (b) 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2; (c) 8.00 mol $NaNO_3$, 6.8×10^2 g $NaNO_3$; (d) 1665 mol CO_2, 73.3 kg CO_2; (e) 18.86 mol CuO, 2.330 kg $CuCO_3$; (f) 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$

45.

(a) 0.0686 mol Mg, 1.67 g Mg; (b) 2.701×10^{-3} mol O_2, 0.08644 g O_2; (c) 6.43 mol $MgCO_3$, 542 g $MgCO_3$ (d) 768 mol H_2O, 13.8 kg H_2O; (e) 16.31 mol BaO_2, 2762 g BaO_2; (f) 0.207 mol C_2H_4, 5.81 g C_2H_4

47.

(a) volume HCl solution $\longrightarrow$ mol HCl $\longrightarrow$ mol $GaCl_3$; (b) 1.25 mol $GaCl_3$, 2.2×10^2 g $GaCl_3$

49.

(a) 5.337×10^{22} molecules; (b) 10.41 g $Zn(CN)_2$

51.

$SiO_2 + 3C \longrightarrow SiC + 2CO$, 4.50 kg SiO_2

53.

5.00×10^3 kg

55.

1.28×10^5 g CO_2

57.

161.4 mL KI solution

59.

176 g TiO_2

61.

The limiting reactant is Cl2.

63.

$\textbf{Percent yield} = 31\%$

65.

$\textbf{g } CCl_4 \longrightarrow \textbf{mol } CCl_4 \longrightarrow \textbf{mol } CCl_2F_2 \longrightarrow \textbf{g } CCl_2F_2, \textbf{ percent yield} = 48.3\%$

67.

$\textbf{percent yield} = 91.3\%$

69.

Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield; 87.6%

71.

The conversion needed is $\textbf{mol Cr} \longrightarrow \textbf{mol } H_3PO_4$. Then compare the amount of Cr to the amount of acid present. Cr is the limiting reactant.

73.

$Na_2C_2O_4$ is the limiting reactant. percent yield = 86.56%

75.

Only four molecules can be made.

77.

This amount cannot be weighted by ordinary balances and is worthless.

79.

3.4×10^{-3} *M* H_2SO_4

81.

9.6×10^{-3} *M* Cl^-

83.

22.4%

85.

The empirical formula is BH_3. The molecular formula is B_2H_6.

87.

49.6 mL

89.

13.64 mL

91.

0.0122 *M*

93.

34.99 mL KOH

95.

The empirical formula is WCl_4.

This page titled 7.5.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

8: Kinetics- Rates of Chemical Reactions

8.1: Chemical Reaction Rates

8.2: Factors Affecting Reaction Rates

8.3: Rate Laws

8.4: Catalysis

8.5: Exercises

8.5.1: Answers to selected Exercises

This page titled 8: Kinetics- Rates of Chemical Reactions is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

8.1: Chemical Reaction Rates

Learning Objectives

By the end of this section, you will be able to:

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

Erroneous nesting of equation structures

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\mathbf{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathbf{H_2O_2}]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t2; and Δ[H2O2] represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\mathbf{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Figure **8.1.1** provides an example of data collected during the decomposition of $\mathbf{H_2O_2}$.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Figure **8.1.1**: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.500mol/L - 1.000mol/L)}{(6.00h - 0.00h)} = 0.0833molL^{-1}h^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.0625mol/L - 0.125mol/L)}{(24.00h - 18.00h)} = 0.010molL^{-1}h^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of $\mathbf{H_2O_2}$ at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 8.1.2). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

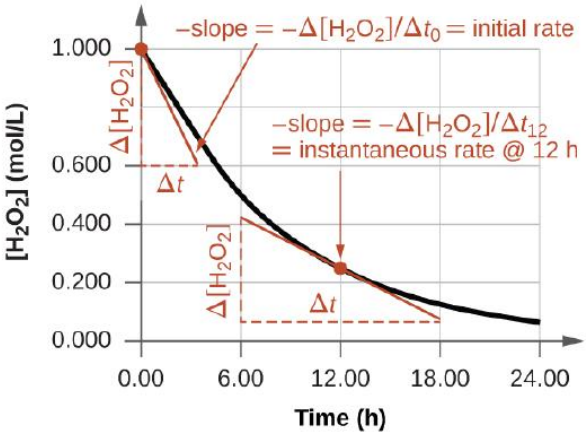


Figure 8.1.2: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life: Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 8.1.3). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

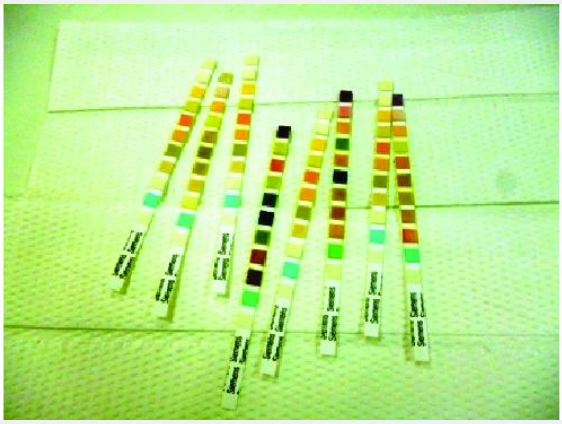


Figure **8.1.3**: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

8.1.1: Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$A \longrightarrow B \tag{8.1.1}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate} = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta mol\ NH_3}{\Delta t} \times \frac{1 mol\ N_2}{2 mol\ NH_3} = \frac{\Delta mol\ N_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta mol\ NH_3}{\Delta t} = \frac{\Delta mol\ N_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are

present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t}$$

Figure 8.1.4: illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6} M/s}{9.70 \times 10^{-7} M/s} \approx 3$$

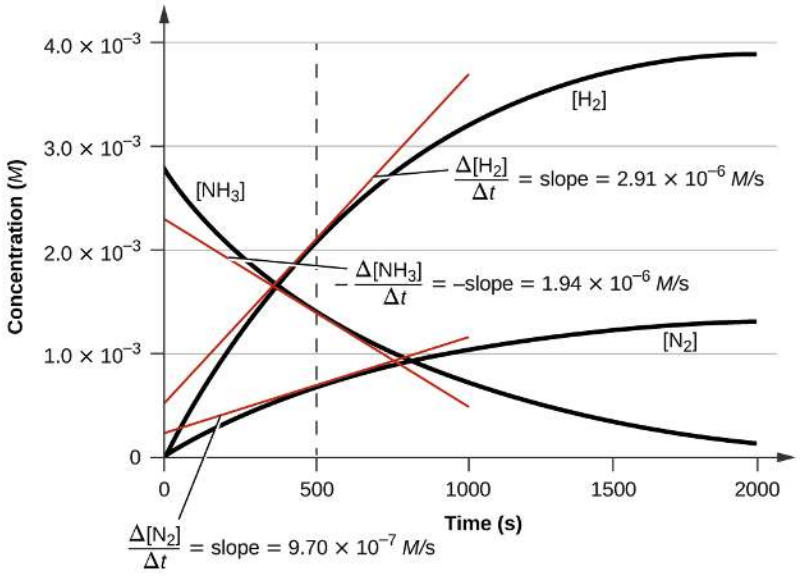


Figure 8.1.4: Changes in concentrations of the reactant and products for the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 8.1.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \tag{8.1.2}$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise 8.1.1

The rate of formation of Br_2 is 6.0 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

Example 8.1.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure **8.1.2**: shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20 10^{-2} mol/L/h, that is:

$$-\frac{1}{2}\frac{\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{1}{2}\frac{\Delta[\mathrm{H_2O}]}{\Delta t} = \frac{\Delta[\mathrm{O_2}]}{\Delta t} \tag{8.1.3}$$

What is the instantaneous rate of production of $\mathbf{H_2O}$ and $\mathbf{O_2}$?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{1}{2}\frac{\Delta[\mathrm{H_2O}]}{\Delta t} = \frac{\Delta[\mathrm{O_2}]}{\Delta t} \tag{8.1.4}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} molL^{-1}h^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2} molL^{-1}h^{-1}$$

Exercise 8.1.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10 10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05 10^{-6} mol/L/s, N_2 and 3.15 10^{-6} mol/L/s, H_2.

This page titled 8.1: Chemical Reaction Rates is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **12.1: Chemical Reaction Rates** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

8.2: Factors Affecting Reaction Rates

Learning Objectives

By the end of this section, you will be able to:

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

8.2.1: The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

8.2.2: The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 8.2.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 8.2.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

8.2.3: Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot

plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

8.2.4: Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure **8.2.2**). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2\,(g) + H_2O\,(g) \longrightarrow H_2SO_3\,(aq)}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3\,(s) + H_2SO_3\,(aq) \longrightarrow CaSO_3\,(aq) + CO_2\,(g) + H_2O\,(l)}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Figure **8.2.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

8.2.5: The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, $\mathrm{H_2O_2}$, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$\mathrm{2\,H_2O_2\,(aq) \longrightarrow 2\,H_2O\,(l) + O_2\,(g)}$$

Under typical conditions, this decomposition occurs very slowly. When dilute $\mathrm{H_2O_2\,(aq)}$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

This page titled 8.2: Factors Affecting Reaction Rates is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **12.2: Factors Affecting Reaction Rates** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

8.3: Rate Laws

Learning Objectives

By the end of this section, you will be able to:

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. Rate laws (sometimes called *differential rate laws*) or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow \text{ products}$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate } = k[A]^m[B]^n$$

in which [*A*] and [*B*] represent the molar concentrations of reactants, and *k* is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents *m* and *n* are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate } = k\,[H_2O_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate } = k\,[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate } = k\,[\text{H}^+]\,[\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 8.3.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2\,(\text{g}) + \text{CO}\,(\text{g}) \longrightarrow \text{NO}\,(\text{g}) + \text{CO}_2\,(\text{g})$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate } = k\,[\text{NO}_2]^m\,[\text{CO}]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

? Exercise 8.3.1*A*

The rate law for the reaction:

$$H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

has been determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

order in NO = 2; order in H_2 = 1; overall order = 3

? Exercise 8.3.1*B*

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

order in CH_3OH = 1; order in $CH_3CH_2OCOCH_3$ = 0; overall order = 1

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

✓ Example 8.3.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 8.3.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

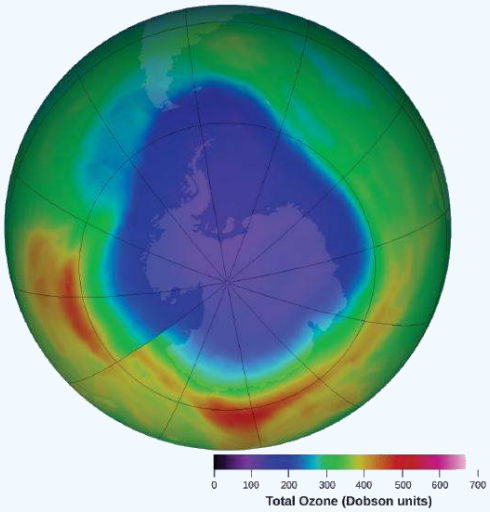


Figure **8.3.1**: A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathbf{NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}\,(\mathrm{mol\,L^{-1}\,s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\mathbf{rate} = k[NO]^m\,[O_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 1:

Determine the value of m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

Step 2:

Determine the value of n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\mathbf{rate} = k[NO]^1\,[O_3]^1 = k[NO]\,[O_3]$$

Step 3:

Determine the value of k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$k = \frac{\text{rate}}{[NO]\,[O_3]}$$
$$= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}}{(1.00 \times 10^{-6}\ \text{mol L}^{-1})\,(3.00 \times 10^{-6}\ \text{mol L}^{-1})}$$
$$= 2.20 \times 10^{7}\ \text{L mol}^{-1}\text{s}^{-1}$$

? Exercise 8.3.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$CH_3CHO\,(g) \longrightarrow CH_4\,(g) + CO\,(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[CH_3CHO]}{\Delta t}$ (mol $L^{-1}s^{-1}$)
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

rate $= k\,[CH_3CHO]^2$ with k = 6.7310^{-6} L/mol/s

8.3.1: Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$NO_2 + CO \longrightarrow NO + CO_2 \qquad \text{rate} = k\,[NO_2]^2$$
$$CH_3\ CHO \longrightarrow CH_4 + CO \qquad \text{rate} = k\,[CH_3CHO]^2$$
$$2\,N_2\ O_5 \longrightarrow NO_2 + O_2 \qquad \text{rate} = k\,[N_2O_5]$$
$$2\,NO_2 + F_2 \longrightarrow 2\,NO_2\ F \qquad \text{rate} = k\,[NO_2]\,[F_2]$$
$$2\,NO_2\ Cl \longrightarrow 2\,NO_2 + Cl_2 \qquad \text{rate} = k\,[NO_2Cl]$$

Note

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example **8.3.2** was determined to be k was derived to be $\text{L mol}^{-1}\text{s}^{-1}$. For the third-order reaction, k was derived to be $\text{L}^2\text{mol}^{-2}\text{s}^{-1}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\text{L}^{x-1}\,\text{mol}^{1-x}\text{s}^{-1}$. Table **8.3.1** summarizes the rate constant units for common reaction orders.

Table **8.3.1**: Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ($L^{x-1}\ mol^{1-x}\ s^{-1}$)
0 (zero)	$mol\ L^{-1}\ s^{-1}$
1 (first)	s^{-1}
2 (second)	$L\ mol^{-1}\ s^{-1}$
3 (third)	$L^2\ mol^{-2}\ s^{-1}$

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

This page titled 8.3: Rate Laws is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **12.3: Rate Laws** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

8.4: Catalysis

Learning Objectives

By the end of this section, you will be able to:

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 8.4.1 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

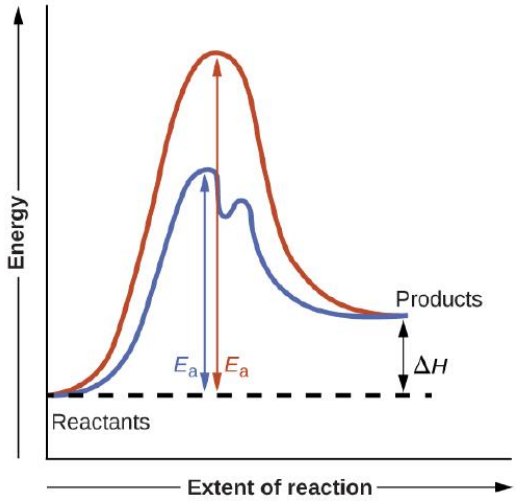
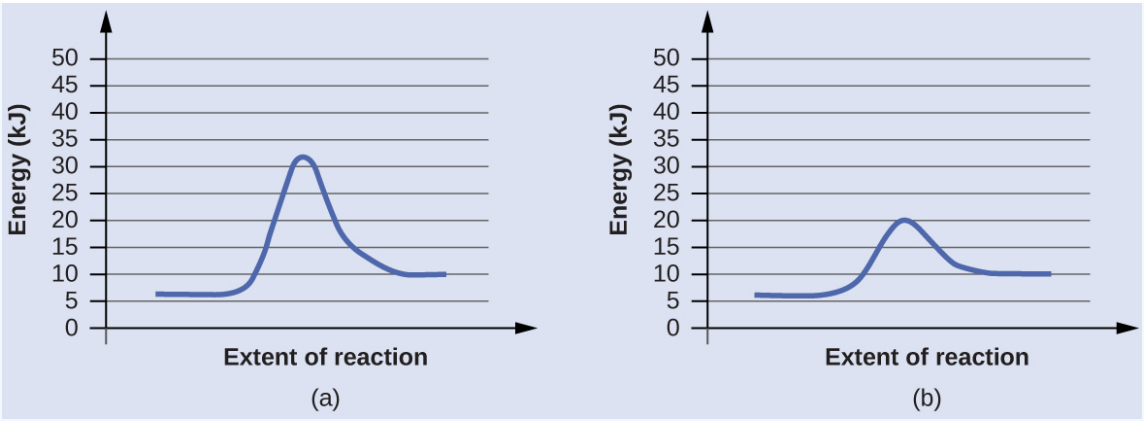


Figure 8.4.1: Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 8.4.1: Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

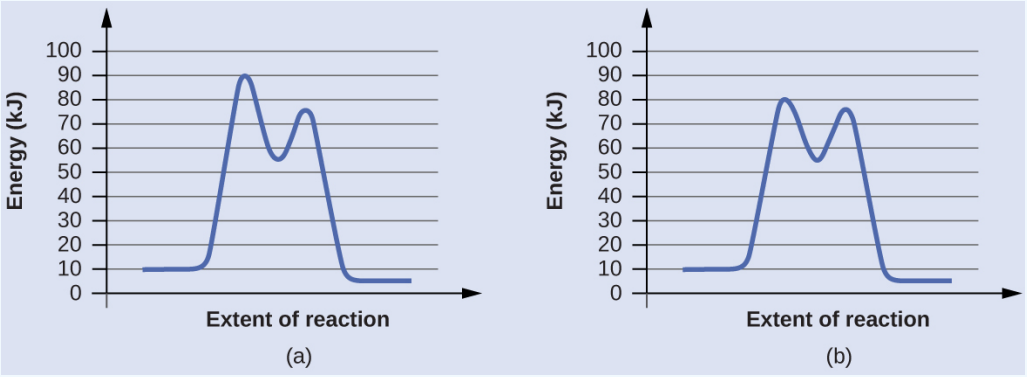
Activation energies are calculated by subtracting the reactant energy from the transition state energy.

$$\text{diagram}(a): E_a = 32kJ - 6kJ = 26kJ$$
$$\text{diagram}(b): E_a = 20kJ - 6kJ = 14kJ$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram b.

Exercise 8.4.1

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

Portrait of a Chemist: Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure **8.4.2**), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

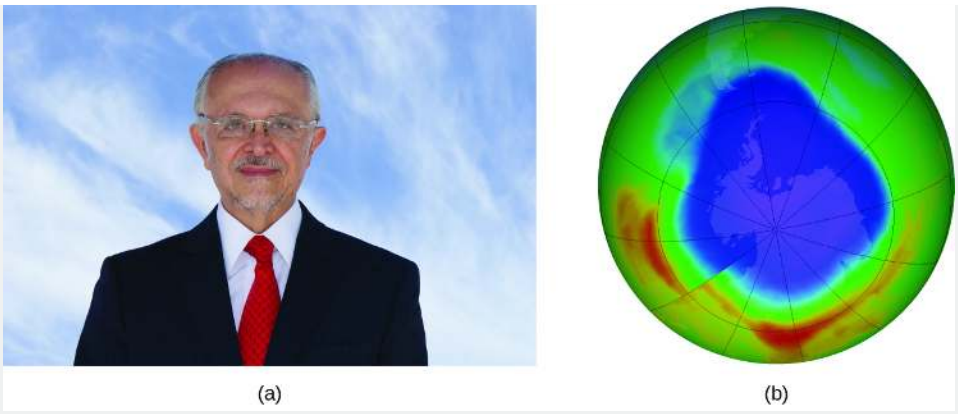


Figure 8.4.2: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

\[CH_3 Cl + OH \longrightarrow Cl +\text { other products }]

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

overall Reaction: $O_3 + O \longrightarrow 2O_2$ \nonumber \]

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 12.21, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 8.4.4).

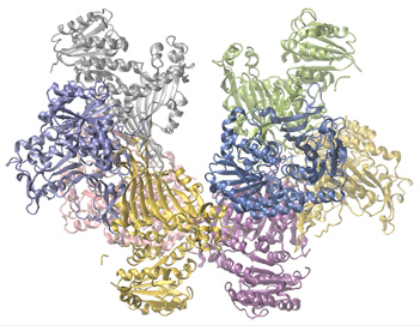


Figure 12.21 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

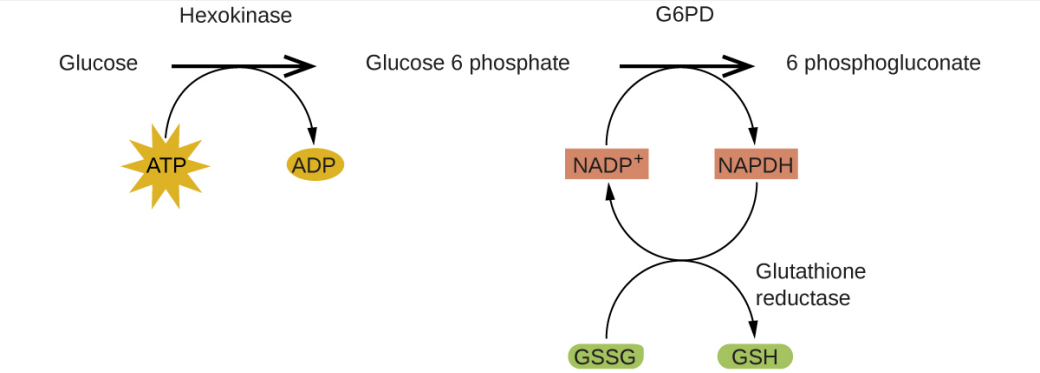


Figure 8.4.4: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Chemistry in Everyday Life: Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 8.4.6).

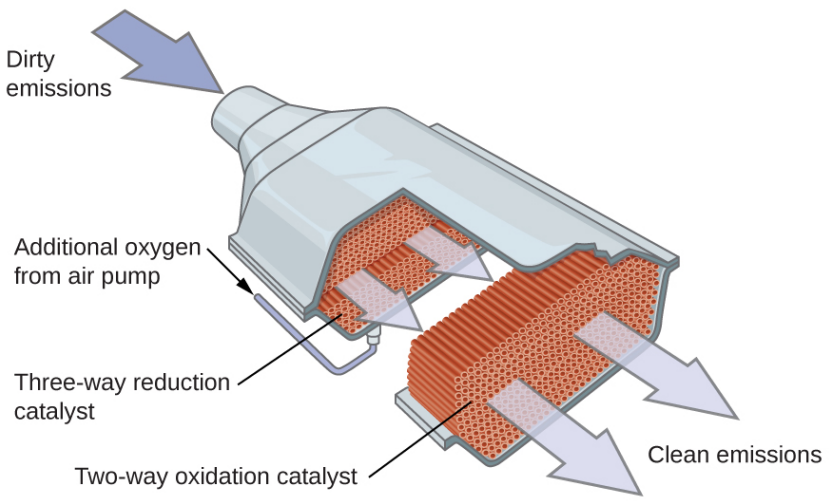


Figure 8.4.6: A catalytic converter allows for the combution of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Link to Learning

The LibreTexts provides a thorough explanation of how catalytic converters work.

How Sciences Interconnect: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 8.4.1.

Table 8.4.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain

how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure **8.4.7**).

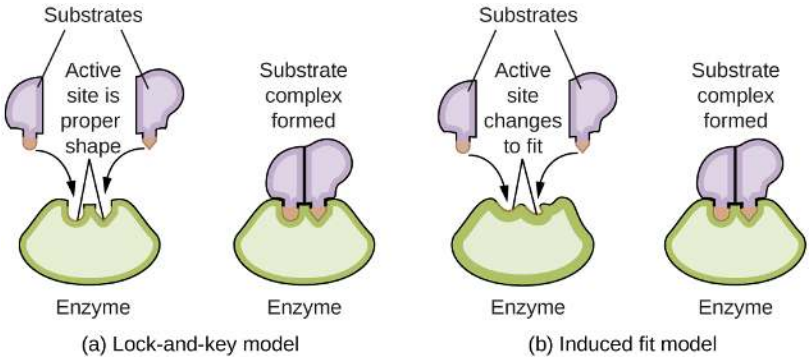


Figure **8.4.7**: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

8.4.1: Footnotes

- 1"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

This page titled 8.4: Catalysis is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **12.7: Catalysis** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

8.5: Exercises

1.

What is the difference between average rate, initial rate, and instantaneous rate?

2.

Ozone decomposes to oxygen according to the equation $\mathbf{2O_3}(g) \longrightarrow \mathbf{3O_2}(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

3.

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $\mathbf{Cl_2}(g) + \mathbf{3F_2}(g) \longrightarrow \mathbf{2ClF_3}(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

4.

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$\mathbf{2C_4H_6} \longrightarrow \mathbf{C_8H_{12}}$

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (M)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

(a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

(b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?

(c) Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

5.

A study of the rate of the reaction represented as $\mathbf{2}\boldsymbol{A} \longrightarrow \boldsymbol{B}$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
$[A]$ (M)	1.00	0.775	0.625	0.465	0.360	0.285	0.230

(a) Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

(b) Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus $[A]$. What are the units of this rate?

(c) Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

6.

Consider the following reaction in aqueous solution:

$\mathbf{5Br^-}(aq) + \mathbf{BrO_3^-}(aq) + \mathbf{6H^+}(aq) \longrightarrow \mathbf{3Br_2}(aq) + \mathbf{3H_2O}(l)$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is 3.5×10^{-4} mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

7.

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

8.

Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

9.

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on "Reload Launcher" and change to "Angled shot" to see the difference.

(a) What happens when the angle of the collision is changed?

(b) Explain how this is relevant to rate of reaction.

10.

In the PhET Reactions & Rates interactive, use the "Many Collisions" tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select "Show bonds" under Options. How is the rate of the reaction affected by concentration and temperature?

11.

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select "Show Bonds" under Options.

(a) Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?

(b) Click "Pause" and then "Reset All," and then enter 15 molecules of A and 10 molecules of BC once again. Select "Show Bonds" under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

12.

How do the rate of a reaction and its rate constant differ?

13.

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

14.

Tripling the concentration of a reactant increases the rate of a reaction nine-fold. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four-fold. What is the order of the reaction with respect to that reactant?

15.

How will the rate of reaction change for the process: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}]^2$?

(a) Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.

(b) Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

16.

How will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k\,[\mathrm{NO_2}]\,[\mathrm{CO}]$?

(a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm

(b) Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

17.

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3×10^{-6} *M* and [O_3] = 5.9×10^{-7} *M*?

18.

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$^{32}_{15}\mathrm{P} \longrightarrow {}^{32}_{16}\mathrm{S} + \mathrm{e}^-$

rate = $4.85 \times 10^{-2}\ \mathrm{day}^{-1}\ [^{32}\mathrm{P}]$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

19.

The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} year^{-1}. The products of the decay are nitrogen atoms and electrons (beta particles):

$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + \mathrm{e}^-$

$\text{rate} = k\,[^{14}_{6}\mathrm{C}]$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5×10^{-9} *M*?

20.

The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55×10^{-4} *M*?

21.

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}

Rate (mol L^{-1} h^{-1})	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate law, the rate constant, and the overall order for this reaction.

22.

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

[NH_3] (M)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol L^{-1} h^{-1})	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate law, the rate constant, and the overall order for this reaction.

23.

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$$

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (M)	0.10	0.20	0.30
Rate (mol L^{-1} h^{-1})	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

24.

From the following data, determine the rate law, the rate constant, and the order with respect to A for the reaction $A \longrightarrow 2C$.

[A] (M)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol L^{-1} h^{-1})	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

25.

Nitrogen monoxide reacts with chlorine according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L)	[Cl_2] (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

26.

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

$$H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol L^{-1} s^{-1})	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

27.

For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol L^{-1} s^{-1})	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

(a) What is the order of the reaction with respect to [*A*], and what is the rate law?

(b) What is the rate constant?

28.

For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{initial}$ (*M*)	0.170	0.212	0.357
Rate (mol L^{-1} s^{-1})	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

(a) What is the order of the reaction with respect to [*Q*], and what is the rate law?

(b) What is the rate constant?

29.

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2×10^{-4} min^{-1}.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

What is the rate of the reaction when [N_2O_5] = 0.40 *M*?

30.

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

(a) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} L^2 mol^{-2} s^{-1}.

31.

The following data have been determined for the reaction:

$$I^- + OCl^- \longrightarrow IO^- + Cl^-$$

	1	2	3
$[I^-]_{initial}$ (M)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (M)	0.050	0.050	0.010
Rate (mol L^{-1} s^{-1})	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate law and the rate constant for this reaction.

32.

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of A at varying times.

33.

Use the data provided to graphically determine the order and rate constant of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4
$[SO_2Cl_2]$ (M)	0.100	0.0896	0.0802	0.0719
Time (s)	2.50×10^4	3.00×10^4	4.00×10^4	
$[SO_2Cl_2]$ (M)	0.0577	0.0517	0.0415	

34.

Pure ozone decomposes slowly to oxygen, $2O_3(g) \longrightarrow 3O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0×10^3	7.6×10^3	1.00×10^4
$[O_3]$ (M)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.66×10^{-6}
Time (h)	1.23×10^4	1.43×10^4	1.70×10^4	
$[O_3]$ (M)	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}	

35.

From the given data, use a graphical method to determine the order and rate constant of the following reaction:
$2X \longrightarrow Y + Z$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[X] (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

36.

What is the half-life for the first-order decay of phosphorus-32? ($^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-$) The rate constant for the decay is 4.85×10^{-2} day^{-1}.

37.

What is the half-life for the first-order decay of carbon-14? ($^{14}_{6}C \longrightarrow {}^{14}_{7}N + e^-$) The rate constant for the decay is 1.21×10^{-4} $year^{-1}$.

38.

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0×10^{-8} L mol^{-1} s^{-1}.

39.

What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L mol^{-1} h^{-1}.

40.

The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L mol^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

41.

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 M. How long will it take for the concentration to drop to 0.0300 M if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

42.

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3×10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate law that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15×10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

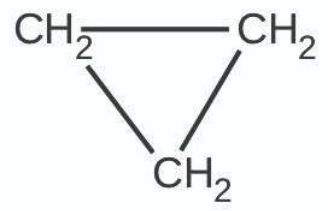
[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

43.

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

44.

There are two molecules with the formula C_3H_6. Propene, $\mathbf{CH_3CH=CH_2}$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4}\ s^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

45.

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the equation is $^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{+1}\mathrm{e}$) Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

(a) What is the rate constant for the decomposition of fluorine-18?

(b) If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?

(c) How long does it take for 99.99% of the ^{18}F to decay?

46.

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

47.

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

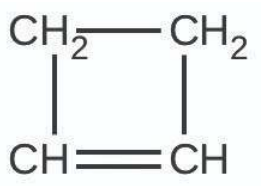
48.

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

49.

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene ($\mathrm{CH_2=CH–CH=CH_2}$) has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as $2.0 \times 10^{-4}\ s^{-1}$ at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

50.

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

51.

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

52.

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

53.

Account for the relationship between the rate of a reaction and its activation energy.

54.

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

55.

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

56.

The rate of a certain reaction doubles for every 10 °C rise in temperature.

(a) How much faster does the reaction proceed at 45 °C than at 25 °C?

(b) How much faster does the reaction proceed at 95 °C than at 25 °C?

57.

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

58.

The rate constant at 325 °C for the decomposition reaction $\mathbf{C_4H_8 \longrightarrow 2C_2H_4}$ is $6.1 \times 10^{-8}\ s^{-1}$, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

59.

The rate constant for the decomposition of acetaldehyde, CH_3CHO, to methane, CH_4, and carbon monoxide, CO, in the gas phase is $1.1 \times 10^{-2}\ L\ mol^{-1}\ s^{-1}$ at 703 K and $4.95\ L\ mol^{-1}\ s^{-1}$ at 865 K. Determine the activation energy for this decomposition.

60.

An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such

reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

61.

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

(a) the change in free energy per second

(b) the change in temperature per second

(c) the number of collisions per second

(d) the number of product molecules

62.

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, k, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (L mol^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

63.

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})
293	0.054
298	0.100

64.

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate law for the disappearance of sucrose: rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

(a) In neutral solution, $k = 2.1 \times 10^{-11}$ s^{-1} at 27 °C and 8.5×10^{-11} s^{-1} at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).

(b) When a solution of sucrose with an initial concentration of 0.150 M reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} M. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.

(c) Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

65.

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

66.

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

67.

Why are elementary reactions involving three or more reactants very uncommon?

68.

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

69.

Define these terms:

(a) unimolecular reaction

(b) bimolecular reaction

(c) elementary reaction

(d) overall reaction

70.

What is the rate law for the elementary termolecular reaction $A + 2B \longrightarrow \text{products?}$ For $3A \longrightarrow \text{products?}$

71.

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a) $Cl_2 + CO \longrightarrow Cl_2CO$
$\text{rate} = k[Cl_2]^{3/2}[CO]$

(b) $PCl_3 + Cl_2 \longrightarrow PCl_5$
$\text{rate} = k[PCl_3][Cl_2]$

(c) $2NO + H_2 \longrightarrow N_2 + H_2O_2$
$\text{rate} = k[NO][H_2]$

(d) $2NO + O_2 \longrightarrow 2NO_2$
$\text{rate} = k[NO]^2[O_2]$

(e) $NO + O_3 \longrightarrow NO_2 + O_2$
$\text{rate} = k[NO][O_3]$

72.

Write the rate law for each of the following elementary reactions:

(a) $O_3 \xrightarrow{\text{sunlight}} O_2 + O$

(b) $O_3 + Cl \longrightarrow O_2 + ClO$

(c) $ClO + O \longrightarrow Cl + O_2$

(d) $O_3 + NO \longrightarrow NO_2 + O_2$

(e) $NO_2 + O \longrightarrow NO + O_2$

73.

Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

What would the rate law be if the mechanism for this reaction were:

$2NO + H_2 \longrightarrow N_2 + H_2O_2$ (slow)

$H_2O_2 + H_2 \longrightarrow 2H_2O$ (fast)

74.

Experiments were conducted to study the rate of the reaction represented by this equation.[3]

$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol L^{-1})	Initial Concentration, [H_2] (mol L^{-1} min^{-1})	Initial Rate of Formation of N_2 (mol L^{-1} min^{-1})
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

(a) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.

(b) Write the overall rate law for the reaction.

(c) Calculate the value of the rate constant, *k*, for the reaction. Include units.

(d) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

(e) The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \rightleftharpoons H_2O + N_2O$

Step 3: $N_2O + H_2 \rightleftharpoons N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

75.

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

$Cl_2(g) \rightleftharpoons 2Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)

$CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)

$COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

(a) Write the overall reaction.

(b) Identify all intermediates.

(c) Write the rate law for each elementary reaction.

(d) Write the overall rate law expression.

76.

Account for the increase in reaction rate brought about by a catalyst.

77.

Compare the functions of homogeneous and heterogeneous catalysts.

78.

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + Cl \longrightarrow O_2 + ClO$$
$$ClO + O \longrightarrow Cl + O_2$$

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2O_3 \longrightarrow 3O_2$$

(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

Is NO a catalyst for the decomposition? Explain your answer.

79.

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction: $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

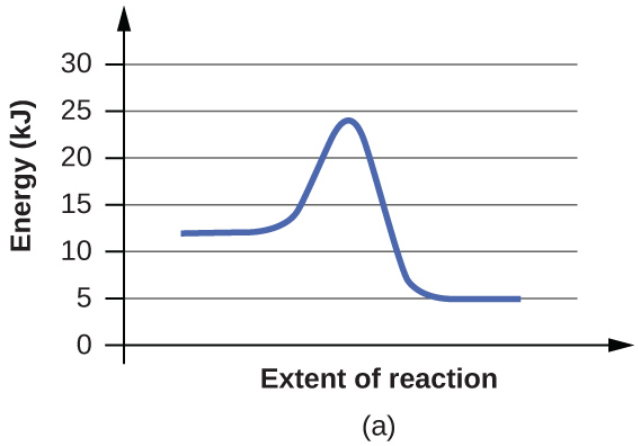
80.

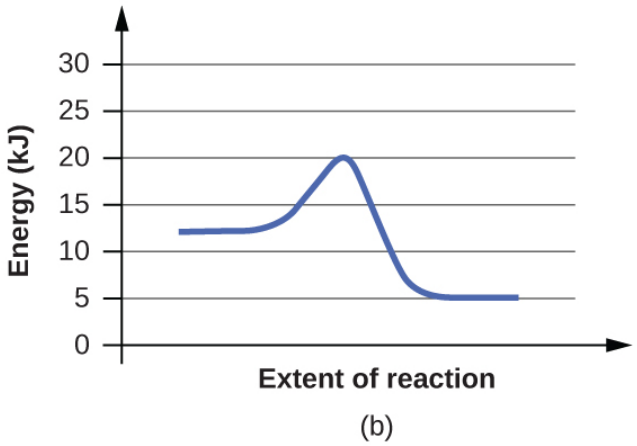
Nitrogen and oxygen react at high temperatures. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

81.

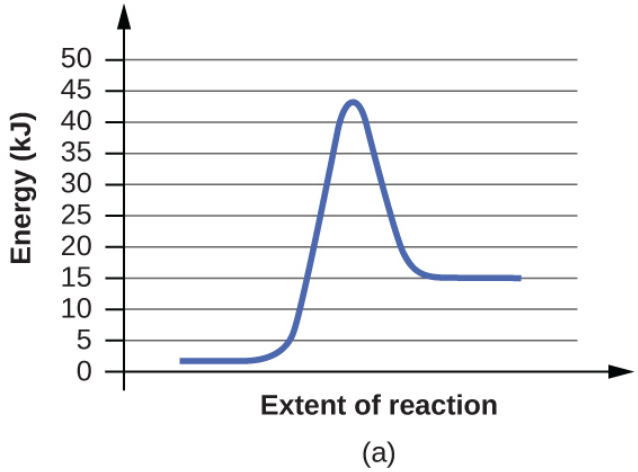
For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

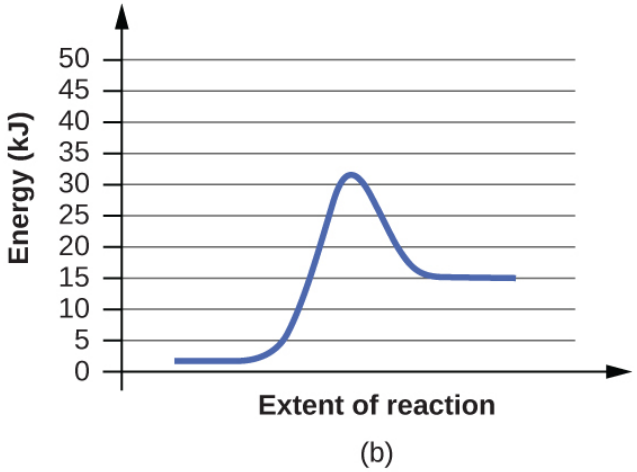
(a)





(b)

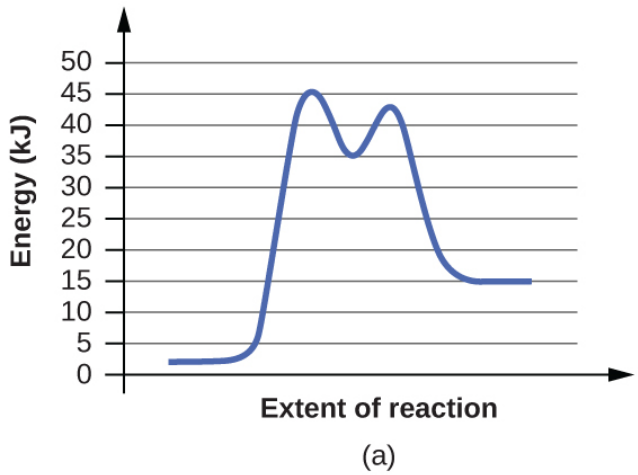


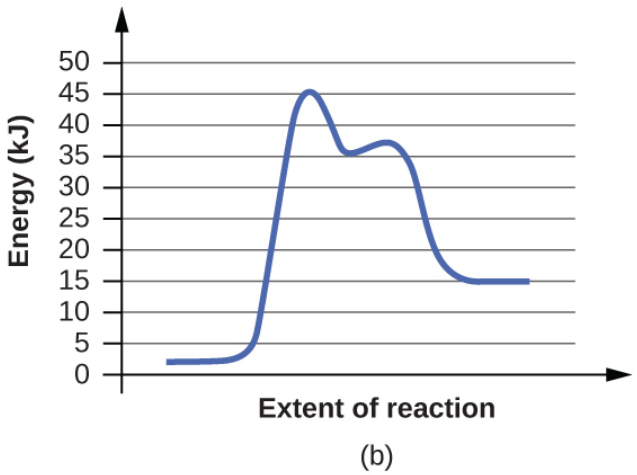


82.

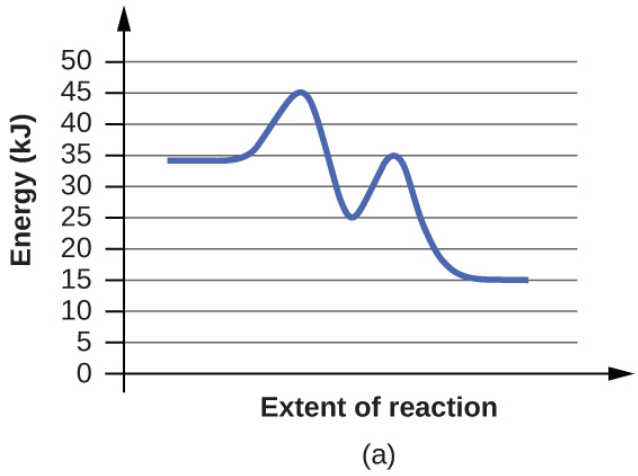
For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

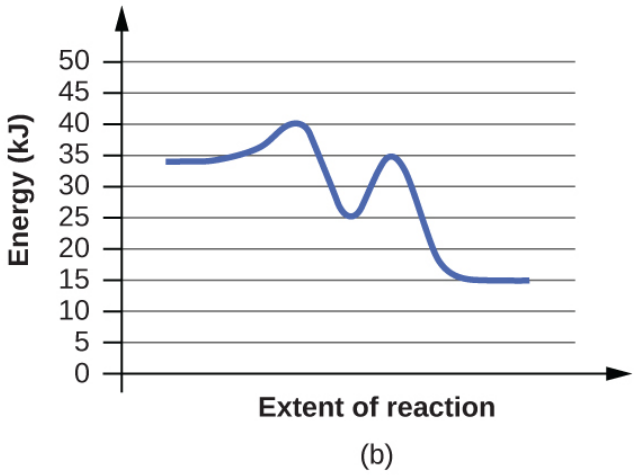
(a)





(b)

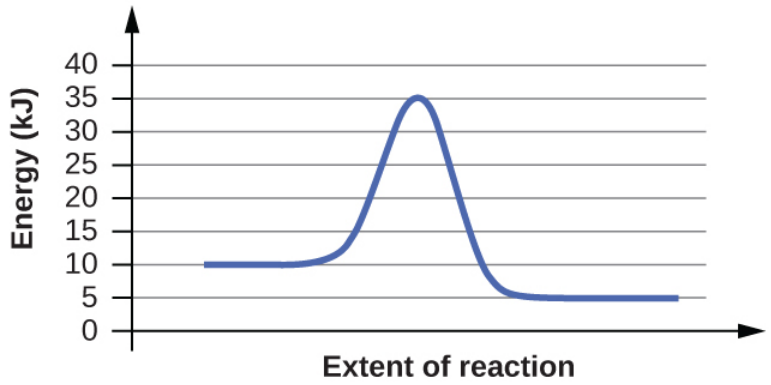




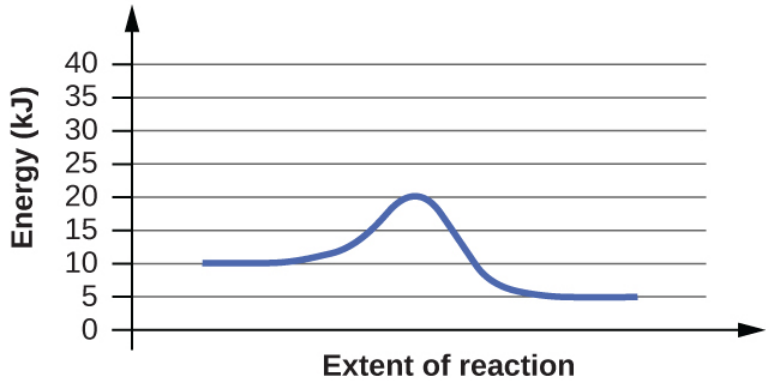
83.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



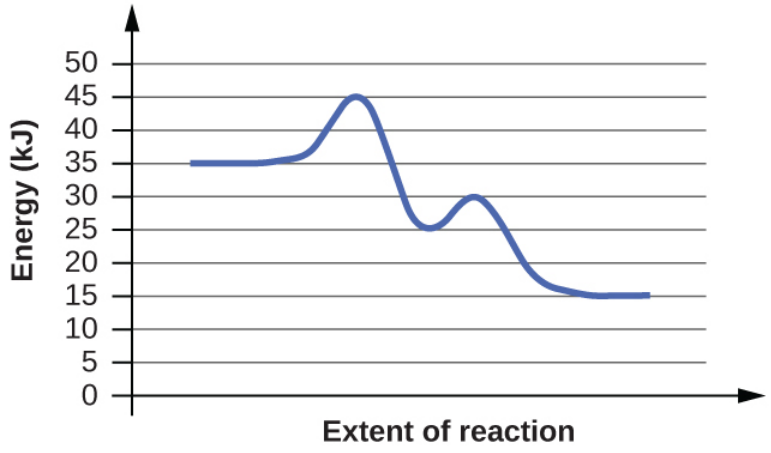
(b)



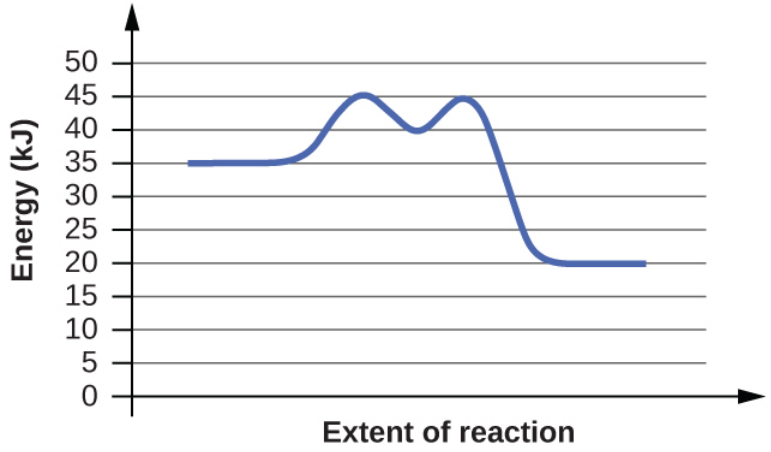
84.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



85.

Assuming the diagrams in Exercise 17.83 represent different mechanisms for the same reaction, which of the reactions has the faster rate?

86.

Consider the similarities and differences in the two reaction diagrams shown in Exercise 17.84. Do these diagrams represent two different overall reactions, or do they represent the same overall reaction taking place by two different mechanisms? Explain your answer.

Footnotes

- 3This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

This page titled 8.5: Exercises is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

8.5.1: Answers to selected Exercises

1.

The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.

3.

$$\text{rate} = +\frac{1}{2}\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$$

5.

(a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 10 − 20 s = 0.0265 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.023 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.012 mol L^{-1} s^{-1}

7.

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

9.

(a) Depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other. (b) Particles of reactant must come into contact with each other before they can react.

11.

(a) very slow; (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

13.

(a) 2; (b) 1

15.

(a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

17.

4.3×10^{-5} mol/L/s

19.

7.9×10^{-13} mol/L/year

21.

rate = *k*; $k = 2.0 \times 10^{-2}$ mol L^{-1} h^{-1} (about 0.9 g L^{-1} h^{-1} for the average male); The reaction is zero order.

23.

rate = $k[\text{NOCl}]^2$; $k = 8.0 \times 10^{-8}$ L/mol/h; second order

25.

rate = $k[\text{NO}]^2[\text{Cl}_2]$; $k = 9.1$ L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

27.

(a) The rate law is second order in A and is written as rate = $k[A]^2$. (b) $k = 7.88 \times 10^{-3}$ L mol^{-1} s^{-1}

29.

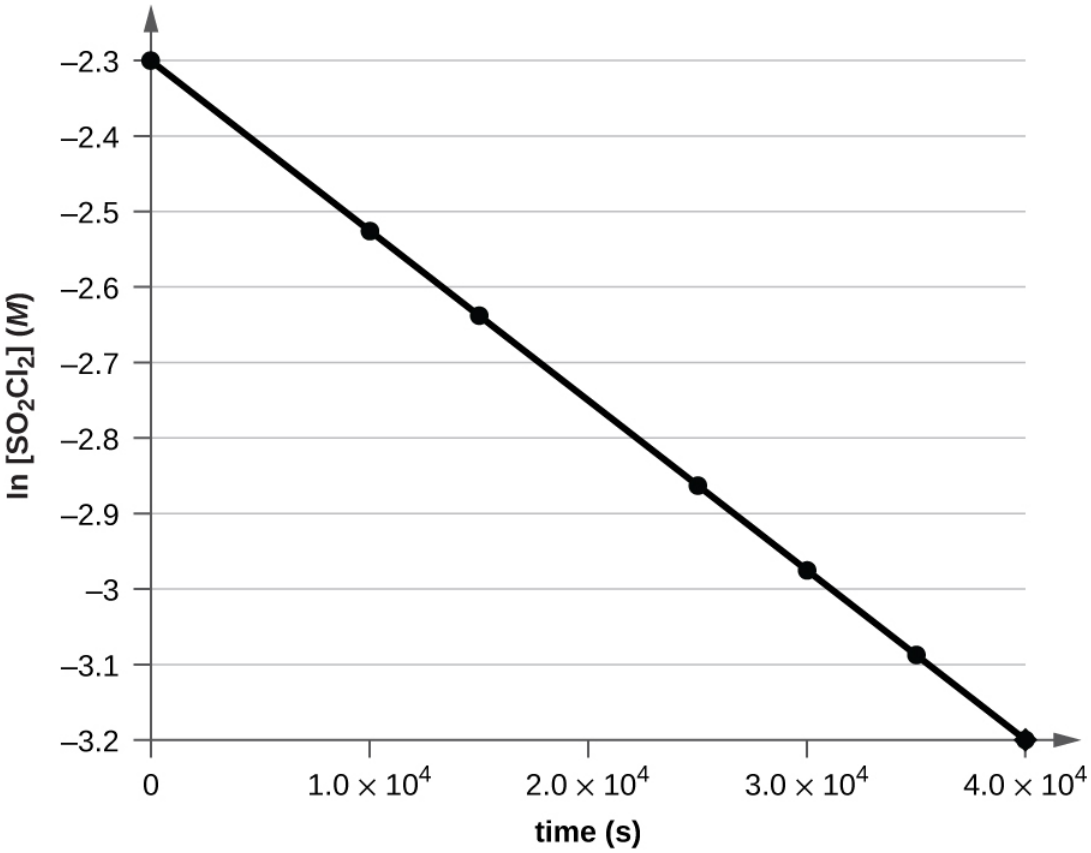
(a) 2.5×10^{-4} mol/L/min

31.

rate = $k[I^-][OCl^-]$; $k = 6.1 \times 10^{-2}$ L mol $^{-1}$ s^{-1}

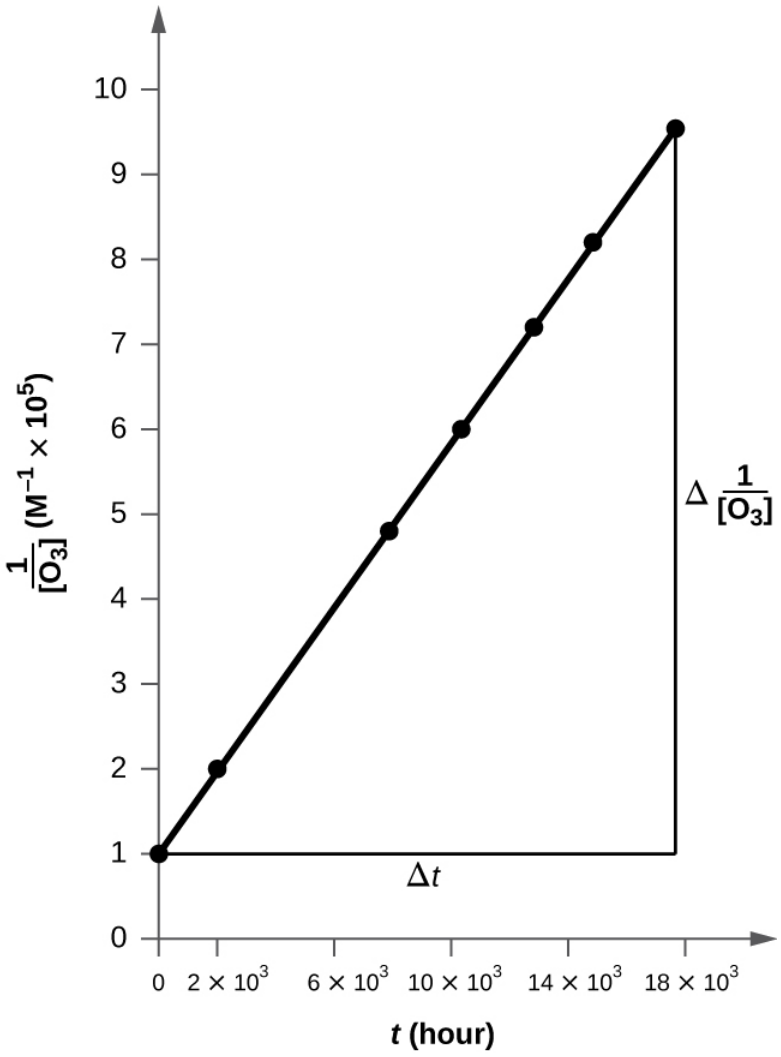
33.

Plotting a graph of $\ln[SO_2Cl_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:



$k = 2.20 \times 10^{-5}$ s^{-1}

34.



The plot is nicely linear, so the reaction is second order. k = 50.1 L mol^{-1} h^{-1}

36.

14.3 d

38.

8.3 × 10^7 s

40.

0.826 s

42.

The reaction is first order. k = 1.0 × 10^7 L mol^{-1} min^{-1}

44.

1.16 × 10^3 s ; 20% remains

46.

252 days

48.

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.53
1.81	2.58
5.33	2.36
4.05	2.47
2.95	2.48
1.72	2.43

50.

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

52.

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

54.

After finding k at several different temperatures, a plot of ln k versus $\frac{1}{T}$, gives a straight line with the slope mfrac from which E_a may be determined.

56.

(a) 4-times faster (b) 128-times faster

58.

$3.9 \times 10^{15}\ s^{-1}$

60.

43.0 kJ/mol

62.

177 kJ/mol

64.

E_a = 108 kJ; $A = 2.0 \times 10^8\ s^{-1}$; $k = 3.2 \times 10^{-10}\ s^{-1}$; (b) 1.81×10^8 h or 7.6×10^6 day; (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

66.

The A atom has enough energy to react with BC; however, the different angles at which it bounces off of BC without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

68.

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate law. Yes. If the reaction is an elementary reaction, then doubling the concentration of A doubles the rate.

70.

Rate = $k[A][B]^2$; Rate = $k[A]^3$

72.

(a) $\text{Rate}_1 = k[O_3]$; (b) $\text{Rate}_2 = k[O_3][Cl]$; (c) $\text{Rate}_3 = k[ClO][O]$; (d) $\text{Rate}_2 = k[O_3][NO]$; (e) $\text{Rate}_3 = k[NO_2][O]$

74.

(a) Doubling $[H_2]$ doubles the rate. $[H_2]$ must enter the rate law to the first power. Doubling [NO] increases the rate by a factor of 4. [NO] must enter the rate law to the second power. (b) $\text{Rate} = k\,[NO]^2[H_2]$; (c) $k = 5.0 \times 10^3\ \text{mol}^{-2}\ \text{L}^{-2}\ \text{min}^{-1}$; (d) 0.0050 mol/L; (e) Step II is the rate-determining step. If step I gives N_2O_2 in adequate amount, steps 1 and 2 combine to give $\mathbf{2NO + H_2 \longrightarrow H_2O + N_2O}$. This reaction corresponds to the observed rate law. Combine steps 1 and 2 with step 3, which occurs by supposition in a rapid fashion, to give the appropriate stoichiometry.

76.

The general mode of action for a catalyst is to provide a mechanism by which the reactants can unite more readily by taking a path with a lower reaction energy. The rates of both the forward and the reverse reactions are increased, leading to a faster achievement of equilibrium.

78.

(a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

79.

no changes.

82.

The lowering of the transition state energy indicates the effect of a catalyst. (a) B; (b) B

84.

The energy needed to go from the initial state to the transition state is (a) 10 kJ; (b) 10 kJ

86.

Both diagrams describe two-step, exothermic reactions, but with different changes in enthalpy, suggesting the diagrams depict two different overall reactions.

This page titled 8.5.1: Answers to selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

9: Equilibrium and Acid Base Chemistry

9.1: Chemical Equilibria
9.2: Equilibrium Constants
9.3: Shifting Equilibria- Le Châtelier's Principle
9.4: Brønsted-Lowry Acids and Bases
9.4.1: Buffers
9.4.2: Acid-Base Titrations
9.5: pH and pOH
9.6: Exercises (Equilibrium)
9.6.1: Chapter 13
9.7: Exercises (Acid-Base)
9.7.1: Answers to Selected Exercises

This page titled 9: Equilibrium and Acid Base Chemistry is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

9.1: Chemical Equilibria

Learning Objectives

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium
- Relate the magnitude of an equilibrium constant to properties of the chemical system

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of “reactant” and “product,” a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 9.1.1 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

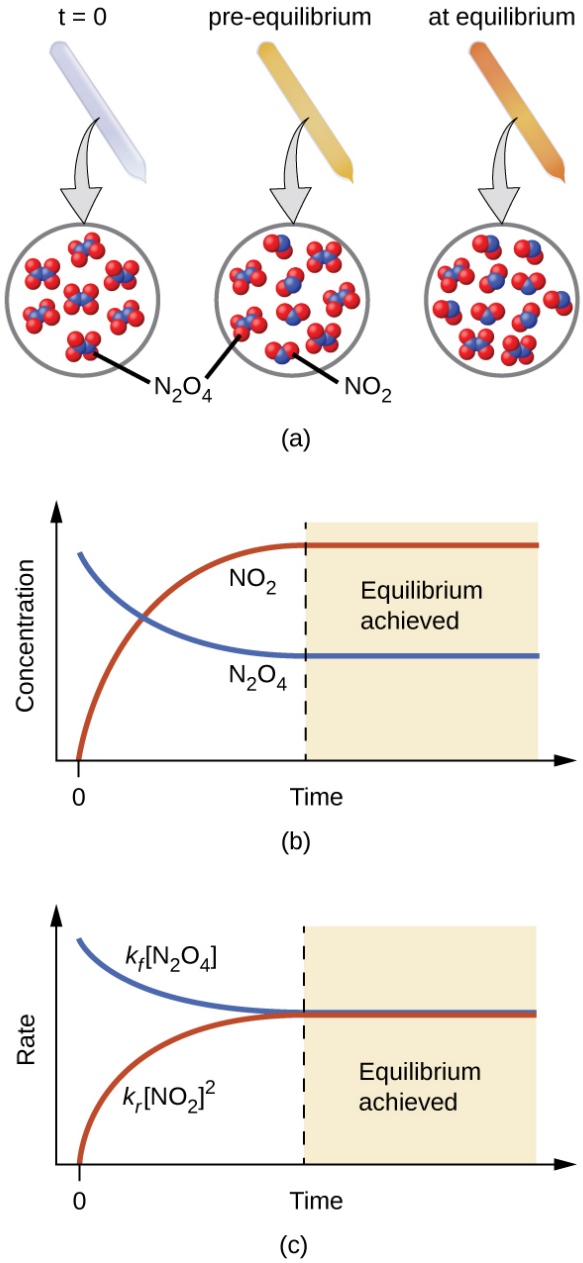


Figure **9.1.1**: (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\text{rate}_f = k_f\,[N_2O_4]$$

$$\text{rate}_r = k_r\,[NO_2]^2$$

As the reaction begins (t = 0), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure **9.1.1***b*). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure **9.1.1***c*). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure **9.1.1***b* and Figure **9.1.1***c*). It's

important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not “stopped,” but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.



Figure **9.1.2**: A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\mathrm{Br_2\,(l) \rightleftharpoons Br_2\,(g)}$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in Figure **9.1.3**.



Figure **9.1.3**: A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

This page titled 9.1: Chemical Equilibria is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **13.1: Chemical Equilibria** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.2: Equilibrium Constants

Learning Objectives

By the end of this section, you will be able to:

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

The status of a reversible reaction is conveniently assessed by evaluating its reaction quotient (Q). For a reversible reaction described by

$$mA + nB + \rightleftharpoons xC + yD$$

the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

where the subscript c denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{P_C^x P_D^y}{P_A{}^m P_B{}^n}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing Q. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

Example 9.2.1: Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

a. $3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)$
b. $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$
c. $4\,NH_3\,(g) + 7\,O_2\,(g) \rightleftharpoons 4\,NO_2\,(g) + 6\,H_2O\,(g)$

Solution

a. $$Q_c = \frac{[O_3]^2}{[O_2]^3}$$

b. $$Q_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

c. $$Q_c = \frac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^7}$$

Exercise 9.2.1

Write the concentration-based reaction quotient expression for each of the following reactions:

a. $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$
b. $C_4H_8\,(g) \rightleftharpoons 2\,C_2H_4\,(g)$
c. $2\,C_4H_{10}\,(g) + 13\,O_2\,(g) \rightleftharpoons 8\,CO_2\,(g) + 10\,H_2O\,(g)$

Answer

a. $$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

b. $$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

c. $$Q_c = \frac{[CO_2]^8\,[H_2O]^{10}}{[C_4H_{10}]^2\,[O_2]^{13}}$$

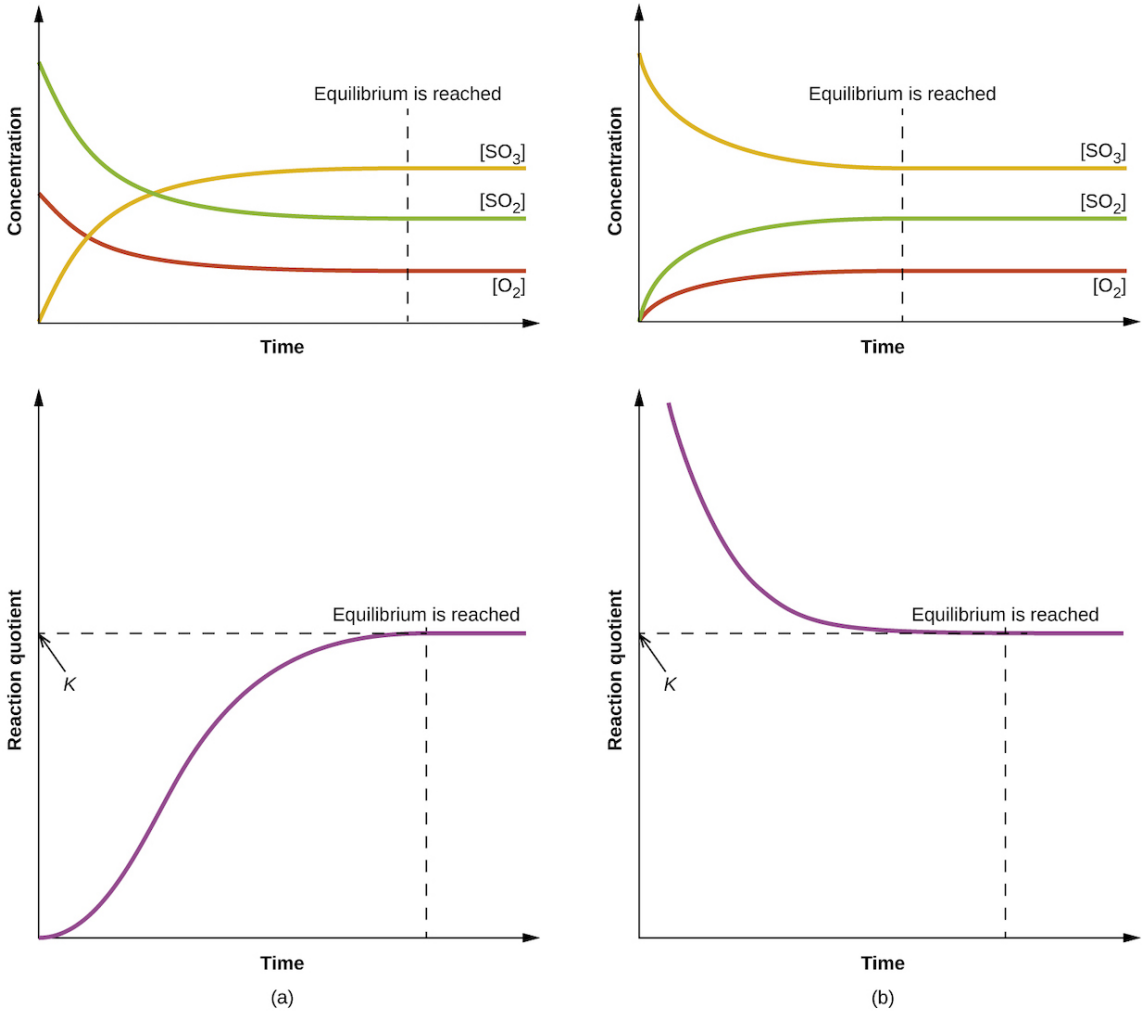


Figure **9.2.1** Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

Two different experimental scenarios are depicted in Figure **9.2.1**, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{0^2}{[SO_2]^2\,[O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the equilibrium constant, K:

$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in Figure **9.2.1** shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**.

Definition: Law of Mass Action

At a given temperature, the reaction quotient for a system at equilibrium is constant.

Example 9.2.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[NO_2]$ = 0.016 *M* and $[N_2O_4]$ = 0.042 *M*.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed

$$[NO_2] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\text{ M}$$

$$[N_2O_4] = 0\text{ M}$$

Thus

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium,

$$K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Exercise 9.2.2

For the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

the equilibrium concentrations are $[SO_2]$ = 0.90 *M*, $[O_2]$ = 0.35 *M*, and $[SO_3]$ = 1.1 *M*. What is the value of the equilibrium constant, K_c?

Answer

K_c = 4.3

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large *K* will reach equilibrium when most of the reactant has been converted to product, whereas a small *K* indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of *K* does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing *Q* to *K* for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \quad K_c = 0.640 \quad T = 800°C$$

The bar charts in Figure **9.2.2** represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

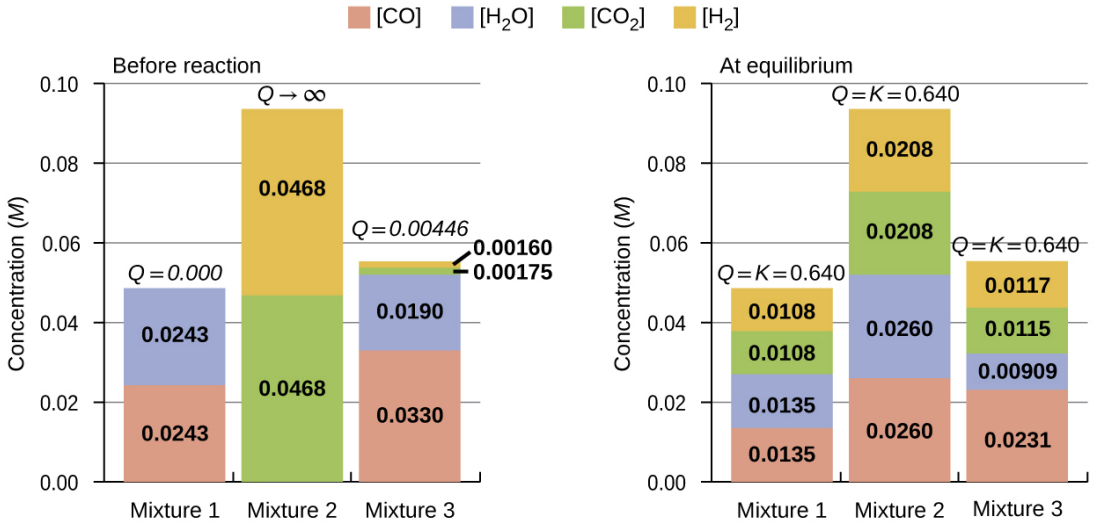


Figure **9.2.2**: Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction

Example 9.2.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) \quad K_c = 0.64$$

https://chem.libretexts.org/@go/page/474925

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040$$

$Q_c < K_c$ (0.040 < 0.64)

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

? Exercise 9.2.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

a. A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2\,NO\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g) \quad K_c = 4.6 \times 10^4$$

b. A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \quad K_c = 0.060$$

c. A 2.00-L flask containing 230 g of SO_3(g):

$$2\,SO_3\,(g) \rightleftharpoons 2\,SO_2\,(g) + O_2\,(g) \quad K_c = 0.230$$

Answer

(a) Q_c = 6.45 \times 10^{3} DELMAR, forward. (b) Q_c = 0.23, reverse. (c) Q_c = 0, forward.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$\mathrm{C_2H_2\,(aq) + 2\,Br_2\,(aq) \rightleftharpoons C_2H_2Br_4\,(aq)} \qquad K_c = \frac{[C_2H_2Br_4]}{[C_2H_2]\,[Br_2]^2}$$

$$\mathrm{I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3{}^-\,(aq)} \qquad K_c = \frac{[I_3-}{[I_2]\,[I^-]}$$

$$\mathrm{HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)} \qquad K_c = \frac{[H_3O^+]\,[F^-]}{[HF]}$$

$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4{}^+\,(aq) + OH^-\,(aq)} \qquad K_c = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the *Q* (or *K*) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

This page titled 9.2: Equilibrium Constants is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

- **13.2: Equilibrium Constants** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.3: Shifting Equilibria- Le Châtelier's Principle

Learning Objectives

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by **Le Chatelier's principle**

Definition: Le Chatelier's Principle

if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

9.3.1: Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad K_c = 50.0 \text{ at } 400^\circ C$$

The rate laws for the forward and reverse reactions are

$$\begin{aligned} &\text{forward} \quad \mathrm{H_2\,(g) + I_2\,(g)} \rightarrow \mathrm{2\,HI\,(g)} && \text{rate}_f = k_f[\mathrm{H_2}]^m[\mathrm{I_2}]^n \\ &\text{reverse} \quad \mathrm{2\,HI\,(g)} \rightarrow \mathrm{H_2\,(g) + I_2\,(g)} && \text{rate}_r = k_r[\mathrm{HI}]^x \end{aligned}$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{rate}_f = \text{rate}_r$$

If the system is stressed by adding reactant, either $\mathrm{H_2}$ or $\mathrm{I_2}$, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\text{rate}_f > \text{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (the equilibrium will shift right). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\text{rate}_f < \text{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}]\,[\mathrm{I_2}]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2 and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the concentrations of all three species will be lower when equilibrium is reestablished. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure P of an ideal gas is proportional to its molar concentration M,

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since

all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)}$$

is described by the reaction quotient

$$Q_P = \frac{(P_{\mathrm{HI}})^2}{P_{\mathrm{H_2}} P_{\mathrm{I_2}}} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$\begin{aligned} Q_p{}' &= \frac{(3P_{HI})^2}{3P_{H_2} 3P_{I_2}} = \frac{9P_{H^2}}{9P_{H_2}P_{I_2}} = \frac{P_{HI^2}}{P_{H_2}P_{I_2}} \\ &= Q_P = K_P \end{aligned}$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system,

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)}$$

however, yields a different result:

$$\begin{aligned} Q_P &= \frac{(P_{NO})^2}{(P_{O_2})}(P_{NO_2})^2 \\ Q'_P &= \frac{(3P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{3(P_{\mathrm{NO_2}})^2} = \frac{9(P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{9(P_{\mathrm{NO_2}})^2} = \frac{27(P_{\mathrm{NO}})^2 P_{\mathrm{O_2}}}{9(P_{\mathrm{NO_2}})^2} \\ &= 3Q_P > K_P \end{aligned}$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better “accommodates” the volume change. In the second example, two moles of reactant (NO_2)

yield three moles of product (2NO + O_2), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

Link to Learning

Check out this link to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Chemistry in Everyday Life: Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestley's approach involved production of carbon dioxide by reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\begin{aligned}
&\textbf{dissolution} && \mathrm{CO_2\,(g) \rightleftharpoons CO_2\,(aq)}\\
&\textbf{hydrolysis} && \mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}\\
&\textbf{ionization} && \mathrm{H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H^+\,(aq)}
\end{aligned}$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to

the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

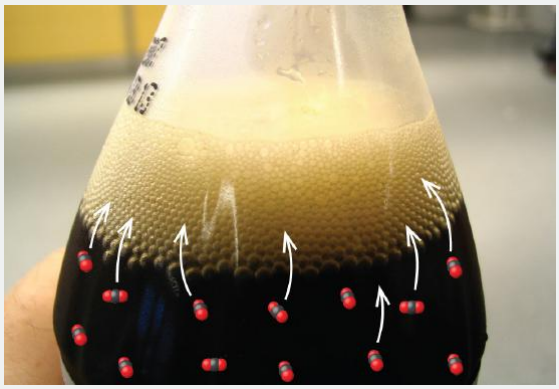


Figure 9.3.1: Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by "D Coetzee"/Flickr)

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."

9.3.2: Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the

equilibrium constant, K. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$A \rightleftharpoons B$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\text{rate}_f = k_f[A]$$
$$\text{rate}_r = k_r[B]$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$k_f[A] = k_r[B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as

described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)} \quad \Delta H = +57.20\ \mathrm{kJ}$$

For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

$$\mathrm{heat + N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

9.3.3: Effect of a Catalyst

The kinetics chapter of this text identifies a *catalyst* as a substance that enables a reaction to proceed via a different mechanism with an accelerated rate. The catalyzed reaction mechanism involves a lower energy transition state than the uncatalyzed reaction, resulting in a lower activation energy, E_a, and a correspondingly greater rate constant.

To discern the effect of catalysis on an equilibrium system, consider the reaction diagram for a simple one-step (elementary) reaction shown in Figure **9.3.2**. The lowered transition state energy of the catalyzed reaction results in lowered activation energies for both the forward and the reverse reactions. Consequently, both forward and reverse reactions are accelerated, and equilibrium is achieved more quickly *but without a change in the equilibrium constant*.

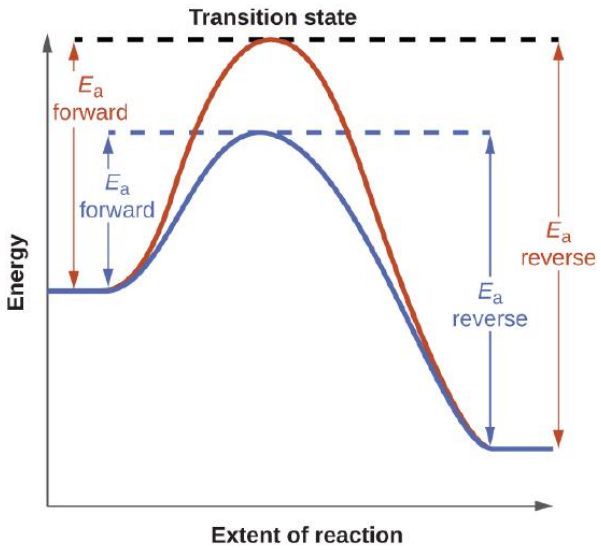


Figure **9.3.2** : Reaction diagrams for an elementary process in the absence (red) and presence (blue) of a catalyst. The presence of catalyst lowers the activation energies of both the forward and reverse reactions but does not affect the value of the equilibrium constant.

An interesting case study highlighting these equilibrium concepts is the industrial production of ammonia, NH_3. This substance is among the "top 10" industrial chemicals with regard to production, with roughly two billion pounds produced annually in the US. Ammonia is used as a chemical feedstock to synthesize a wide range of commercially useful compounds, including fertilizers, plastics, dyes, and explosives.

Most industrial production of ammonia uses the Haber-Bosch process based on the following equilibrium reaction:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \quad \Delta H = -92.2\ \mathrm{kJ}$$

The traits of this reaction present challenges to its use in an efficient industrial process. The equilibrium constant is relatively small (Kp on the order of 10^{-5} at 25 °C), meaning very little ammonia is present in an equilibrium mixture. Also, the rate of this reaction is relatively slow at low temperatures. To raise the yield of ammonia, the industrial process is designed to operate under conditions favoring product formation:

- High pressures (concentrations) of reactants are used, ~150−250 atm, to shift the equilibrium right, favoring product formation.
- Ammonia is continually removed (collected) from the equilibrium mixture during the process, lowering its concentration and also shifting the equilibrium right.
- Although low temperatures favor product formation for this exothermic process, the reaction rate at low temperatures is inefficiently slow. A catalyst is used to accelerate the reaction to reasonable rates at relatively moderate temperatures (400−500 °C).

A diagram illustrating a typical industrial setup for production of ammonia via the Haber-Bosch process is shown in Figure **9.3.3**.

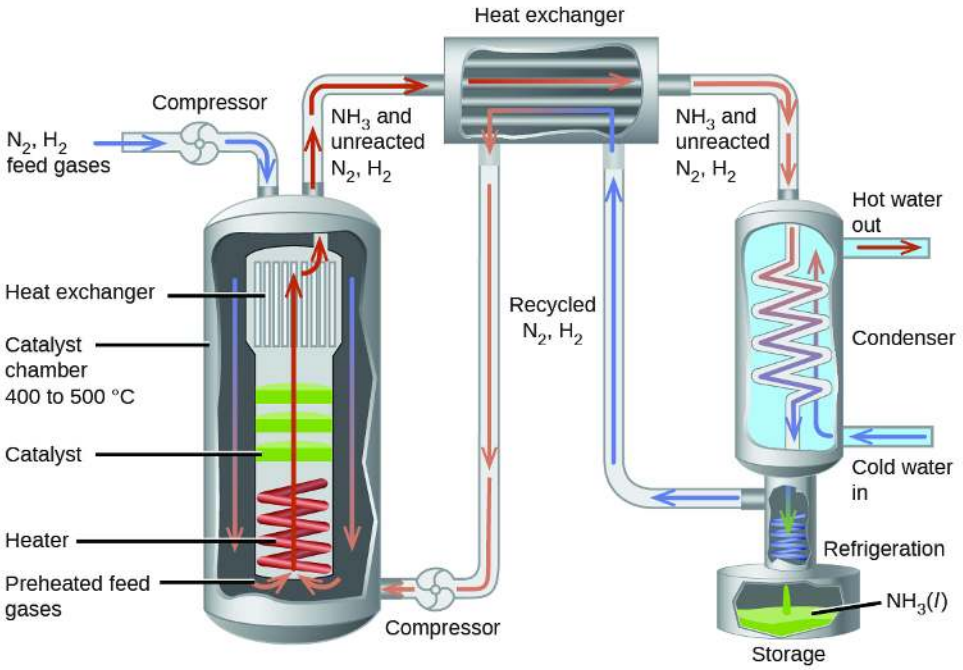


Figure **9.3.3**: The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favor product formation.

This page titled 9.3: Shifting Equilibria- Le Châtelier's Principle is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **13.3: Shifting Equilibria - Le Chatelier's Principle** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.4: Brønsted-Lowry Acids and Bases

Learning Objectives

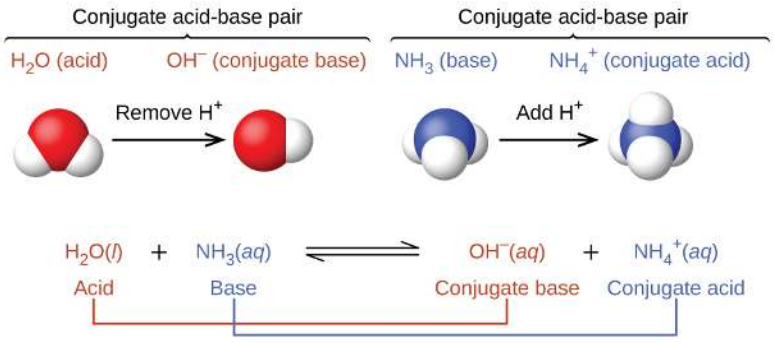
By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

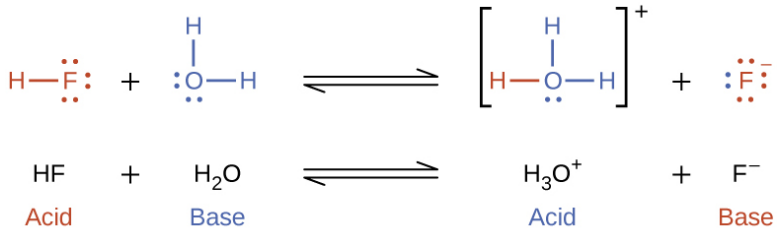
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.) 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. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

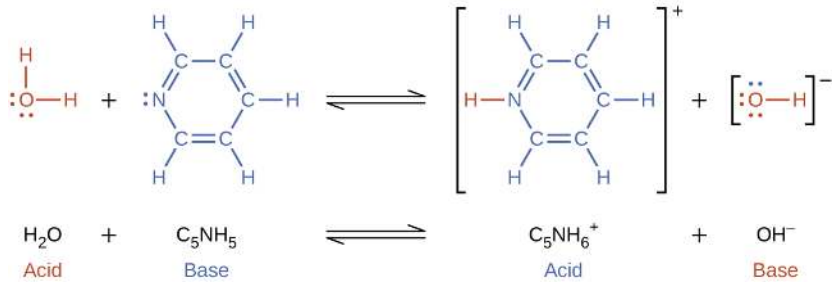
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, NH_4^+, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an 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 transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



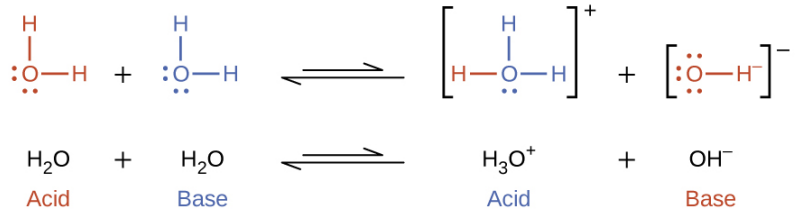
The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:



The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w:

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{9.4.1}$$

with

$$K_w = [H_3O^+][OH^-] \tag{9.4.2}$$

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 about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 9.4.1: 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, $[H_3O^+] = [OH^-] = x$. At 25 °C:

$$K_w = [H_3O^+]\,[OH^-] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

$$x = [H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, $1.0 \times 10^{-7}\,M$.

Exercise 9.4.1

The ion product of water at 80 °C is 2.4 \times 10^{−13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\,M$$

Example 9.4.2: The Inverse Relation between $[H_3O^+]$ and $[OH^-]$

A solution of an acid 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

Use the value of the ion-product constant for water at 25 °C (Equations 9.4.1 and 9.4.2) to calculate the missing equilibrium concentration.

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

with $K_w = [H_3O^+][OH^-]$.

Rearrangement of the K_w expression shows that $[OH^-]$ is inversely proportional to $[H_3O^+]$:

$$K_w = [H_3O^+]\,[OH^-] = (2.0 \times 10^{-6})\,(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Chatelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 9.4.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11}\ M$$

Example 9.4.3: Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

Exercise 9.4.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer

a. $H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$
b. $H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$

This page titled 9.4: Brønsted-Lowry Acids and Bases is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **14.1: Brønsted-Lowry Acids and Bases** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.4.1: Buffers

Learning Objectives

By the end of this section, you will be able to:

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure **9.4.1.1**). A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).



Figure **9.4.1.1**: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

9.4.1.1: How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, strong base added to this solution will neutralize hydronium ion, causing the acetic acid ionization equilibrium to shift to the right and generate additional amounts of the weak conjugate base (acetate ion):

$$\mathrm{CH_3\ CO_2\ H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3\ CO_2^-\,(aq)}$$

Likewise, strong acid added to this buffer solution will shift the above ionization equilibrium left, producing additional amounts of the weak conjugate acid (acetic acid). Figure **9.4.1.2** provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

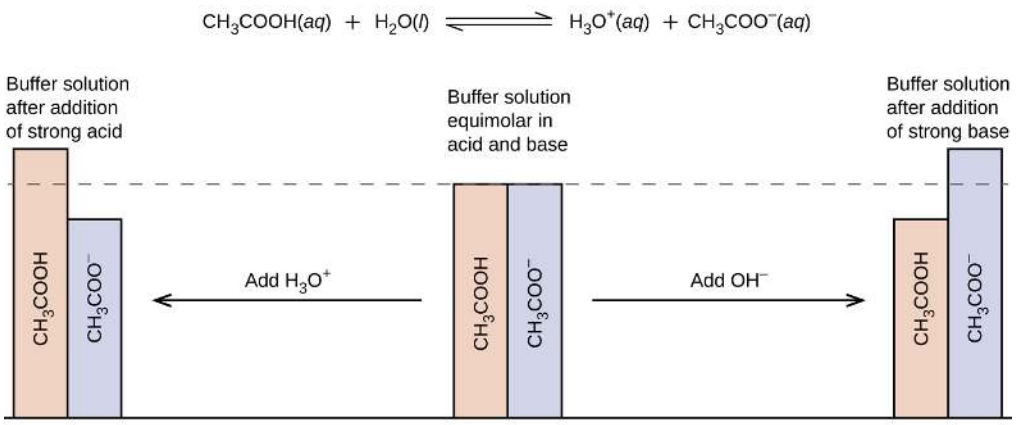


Figure 9.4.1.2: Buffering action in a mixture of acetic acid and acetate salt.

Example 14.20: pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 NaOH is added to 100 mL of this buffer.
c. For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

	CH_3CO_2H +	H_2O ⇌	H_3O^+ +	$CH_3CO_2^-$
Initial concentration (*M*)	0.10		~0	0.10
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$		x	$0.10 + x$

Substituting the equilibrium concentration terms into the K_a expression, assuming $x \ll 0.10$, and solving the simplified equation for x yields

$$x = 1.8 \times 10^{-5}\ \text{M}$$

$$[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5}\ \text{M}$$

$$\begin{aligned} pH &= -\log[\text{H}_3\text{O}^+] \\ &= -\log\left(1.8 \times 10^{-5}\right) \\ &= 4.74 \end{aligned}$$

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer.

Adding strong base will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$0.0010\ \cancel{\text{L}} \times \left(\frac{0.10\ \text{mol NaOH}}{1\ \cancel{\text{L}}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100 \cancel{L} \times \left(\frac{0.100 \text{ mol } CH_3CO_2H}{1 \cancel{L}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The amount of acetic acid remaining after some is neutralized by the added base is

$$\left(1.0 \times 10^{-2}\right) - \left(0.01 \times 10^{-2}\right) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$\left(1.0 \times 10^{-2}\right) + \left(0.01 \times 10^{-2}\right) = 1.01 \times 10^{-2} \text{ mol } NaCH_3CO_2$$

Compute molar concentrations for the two buffer components:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M}$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \text{ M}$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydronium ion initially present in the solution is

$$[H_3O^+] = 10^{-4.74} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{mol } H_3O^+ = (0.100 \text{ L})\left(1.8 \times 10^{-5} \text{ M}\right) = 1.8 \times 10^{-6} \text{ mol } H_3O^+$$

The amount of hydroxide ion added to the solution is

$$molOH^- = (0.0010L)(0.10M) = 1.0 \times 10^{-4} molOH^-$$

The added hydroxide will neutralize hydronium ion via the reaction

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(l)$$

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

$$1.0 \times 10^{-4} mol - 1.8 \times 10^{-6} mol = 9.8 \times 10^{-5} molOH^-$$

corresponding to a hydroxide molarity of

$$\frac{9.8 \times 10^{-5} \text{ mol } OH^-}{0.101 \text{ L}} = 9.7 \times 10^{-4} M$$

The pH of the solution is then calculated to be

$$pH = 14.00 - pOH = 14.00 - -\log\left(9.7 \times 10^{-4}\right) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

? Exercise 9.4.1.1

Show that adding 1.0 mL of $0.10 \text{ M } HCl$ changes the pH of 100 mL of a $1.8 \times 10^{-5} \text{ M } HCl$ solution from 4.74 to 3.00.

Answer

Initial pH of $1.8 \times 10^{-5} \text{ M } HCl$;

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$$

Moles of H_3O^+ in 100 mL 1.8×10^{-5} M HCl;

$$(1.8 \times 10^{-5} \text{ moles/L}) \times (0.100 \text{ L} = 1.8 \times 10^{-6} \text{ mol}$$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl:

$$(0.10 \text{ moles/L}) \times (0.0010 \text{ L}) = 1.0 \times 10^{-4} \text{ mol}$$

Final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$pH = -\log\left[\text{H}_3\text{O}^+\right] = -\log\left(\frac{\text{total moles } \text{H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} mol + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

9.4.1.2: Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure **9.4.1.3**). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.



Figure **9.4.1.3**: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

9.4.1.3: Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure **9.4.1.4** shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

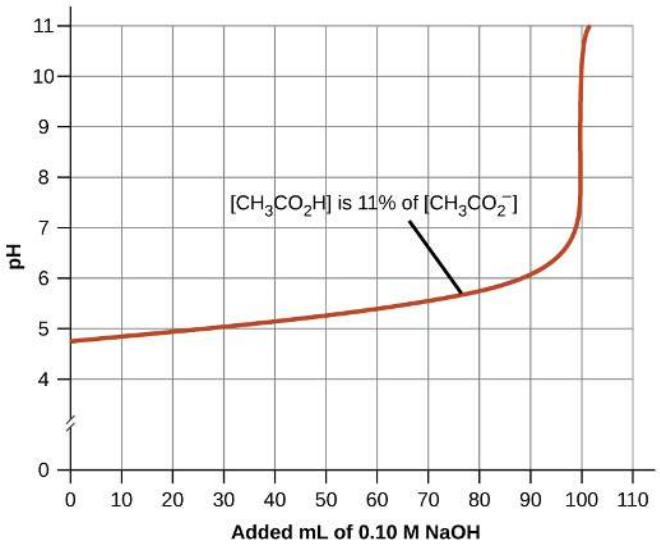


Figure **9.4.1.4**: Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H]$ = 0.10 *M* and Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, $\mathbf{H_2CO_3}$, and the bicarbonate ion, $\mathbf{HCO_3^-}$. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$\mathbf{H_3O^+\,(aq) + HCO_3^-\,(aq) \longrightarrow H_2\,CO_3\,(aq) + H_2O\,(l)}$$

An added hydroxide ion is removed by the reaction:

$$\mathbf{OH^-\,(aq) + H_2CO_3\,(aq) \longrightarrow HCO_3^-\,(aq) + H_2O\,(l)}$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to HCO_3^-). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

9.4.1.4: The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[\mathbf{H_3O^+}]\,[\mathbf{A^-}]}{[\mathbf{HA}]}$$

Rearranging to solve for $[H_3O^+]$ yields:

$$[\mathbf{H_3O^+}] = K_a \times \frac{[\mathbf{HA}]}{[\mathbf{A^-}]}$$

Taking the negative logarithm of both sides of this equation gives

$$-\log\,[\mathbf{H_3O^+}] = -\log K_a - \log \frac{[\mathbf{HA}]}{[\mathbf{A^-}]}$$

which can be written as

$$pH = pK_a + \log \frac{[\mathbf{A^-}]}{[\mathbf{HA}]}$$

where pK_a is the negative of the logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch equation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

Portrait of a Chemist: Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

How Sciences Interconnect: Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2\,(g) + 2\,H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)}$$

The concentration of carbonic acid, $\mathrm{H_2CO_3}$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$pH = pK_a + \log\frac{[\text{ base }]}{[\text{ acid }]} = 6.4 + \log\frac{0.024}{0.0012} = 7.7$$

The fact that the $\mathrm{H_2CO_3}$ concentration is significantly lower than that of the $\mathrm{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Link to Learning

View information on the buffer system encountered in natural waters.

This page titled 9.4.1: Buffers is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **14.6: Buffers** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.4.2: Acid-Base Titrations

Learning Objectives

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

9.4.2.1: Titration Curves

A titration curve is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the computation of pH for a titration solution after additions of several specified titrant volumes. The first example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH. The second example addresses a weak acid titration requiring equilibrium calculations.

Example 9.4.2.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH (the titration curve is shown in Figure 9.4.2.1). Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 *M*. The pH of the solution is then

$$\mathrm{pH} = -\log(0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the initial amount and then dividing by the solution volume:

$$[\mathrm{H_3O^+}] = \frac{n(\mathrm{H^+})}{V} = \frac{0.002500\ \mathrm{mol} \times \left(\frac{1000\ mL}{1\ L}\right) - 0.100\ M \times 12.50\ mL}{25.00\ mL + 12.50\ mL} = 0.0333\ M$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

$$n(OH^-)_0 > n(H^+)_0$$

$$[OH^-] = \frac{n(OH^-)}{V} = \frac{0.100\ M \times 37.50\ mL - 0.002500\ mol \times \left(\frac{1000\ mL}{1\ L}\right)}{25.00\ mL + 37.50\ mL} = 0.0200\ M$$

$$pH = 14 - pOH = 14 + \log([OH^-]) = 14 + \log(0.0200) = 12.30$$

? Exercise 9.4.2.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

Answer

0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

✓ Example 9.4.2.2: Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$$

Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

a. 0.00 mL
b. 25.00 mL
c. 12.50 mL
d. 37.50 mL

Solution

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[H3O^+]\,[CH_3CO_2^-]}{[CH_3CO_2H]} \approx \frac{[H3O^+]^2}{[CH_3CO_2H]_0}$$

and

$$[H3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log\left(1.3 \times 10^{-3}\right) = 2.87$$

(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

$$\frac{0.00250\ mol}{0.0500\ L} = 0.0500\ M\ CH_3CO_2^-$$

Base ionization of acetate is represented by the equation

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

$$K_b = \frac{[H^+]\,[OH^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming $x \ll 0.0500$, the pH may be calculated via the usual ICE approach:

$$K_b = \frac{x^2}{0.0500M}$$

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$\text{pOH} = -\log\left(5.3 \times 10^{-6}\right) = 5.28$$
$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{ Base }]}{[\text{ Acid }]} = -\log\left(K_a\right) + \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = -\log\left(1.8 \times 10^{-5}\right) + \log(1)$$

$$pH = -\log\left(1.8 \times 10^{-5}\right) = 4.74$$

(pH = pK_a at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

$$[OH^-] = \frac{(0.003750mol - 0.00250mol)}{0.06250L} = 2.00 \times 10^{-2}M$$

$$\text{pOH} = -\log\left(2.00 \times 10^{-2}\right) = 1.70$$
$$\text{pH} = 14.00 - 1.70 = 12.30$$

? Exercise 9.4.2.1

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

Answer

0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Performing additional calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in Table **9.4.2.1** and plotted as titration curves in Figure **9.4.2.1**. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

- initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH
- pre-equivalence point (0 mL < *V* < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction product, its conjugate base
- equivalence point (*V* = 25 mL): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid
- postequivalence point (*V* > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

Table **9.4.2.1**: pH Values in the Titrations of a Strong Acid and of a Weak Acid

Volume of 0.100 *M* NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 *M* HCl[1]	pH Values 0.100 *M* CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

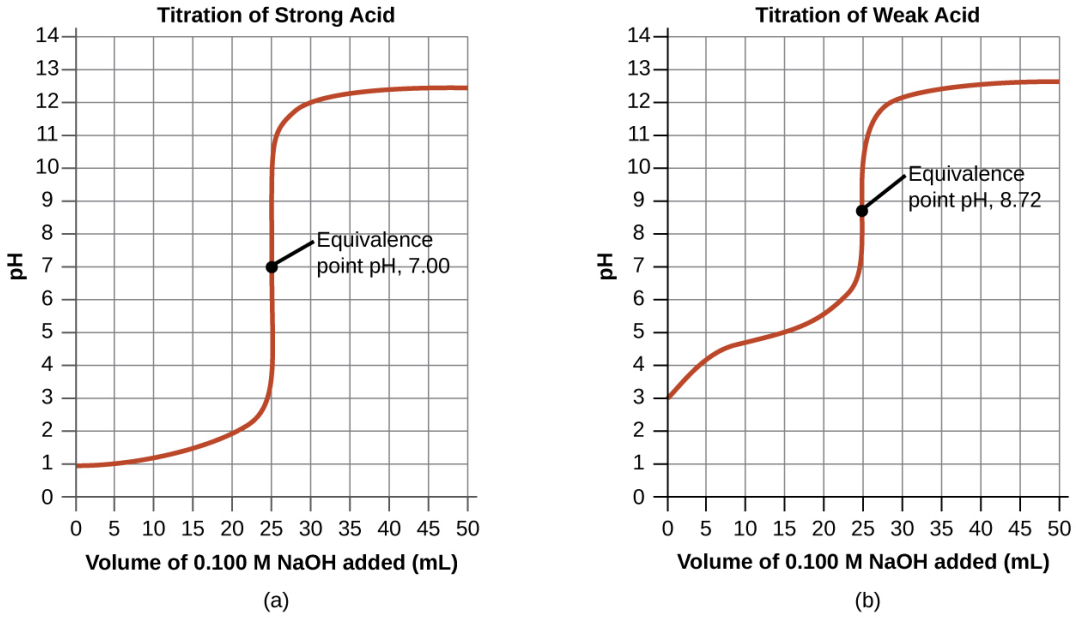


Figure **9.4.2.1**: (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

9.4.2.2: Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than $\mathbf{5.0 \times 10^{-9}\ M}$ (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than $\mathbf{5.0 \times 10^{-9}\ M}$ (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underset{\text{red}}{\mathbf{HIn\,(aq)}} + \mathbf{H_2O\,(l)} \rightleftharpoons \underset{\text{yellow}}{\mathbf{H_3O^+\,(aq)}} + \mathit{In}^-(aq)$$

$$K_a = \frac{[\mathbf{H_3O^+}]\,[\mathbf{In^-}]}{[\mathbf{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathbf{In^-}$, is yellow, and the nonionized form, **HIn**, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species $\mathbf{In^-}$ and **HIn**. If most of the indicator (typically about 60−90% or more) is present as $\mathbf{In^-}$, the perceived color of the solution is yellow. If most is present as **HIn**, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

$$pH = pKa + \log\left(\frac{[\mathbf{In^-}]}{[\mathbf{HIn}]}\right)$$

In solutions where pH > pK_a, the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When pH < pK_a, the log term must be negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pKa, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The **color change interval** (or *pH interval*) for an acid-

base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately pK_a ± 1.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure **9.4.2.2** presents several indicators, their colors, and their color-change intervals.

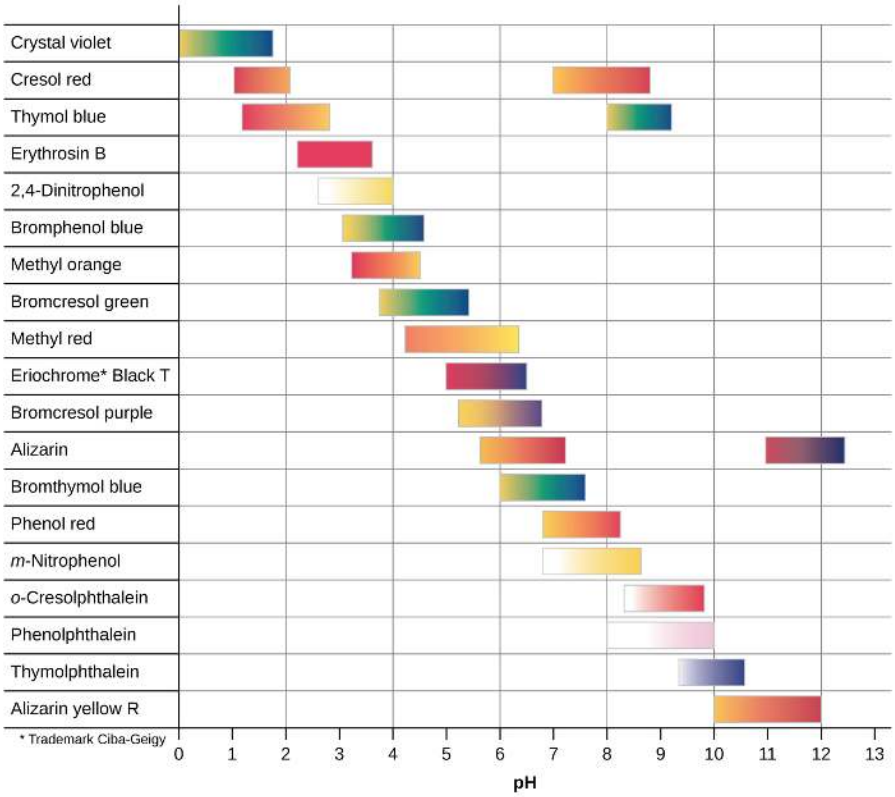


Figure **9.4.2.2**: This chart illustrates the color change intervals for several acid-base indicators.

The titration curves shown in Figure **9.4.2.3** illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

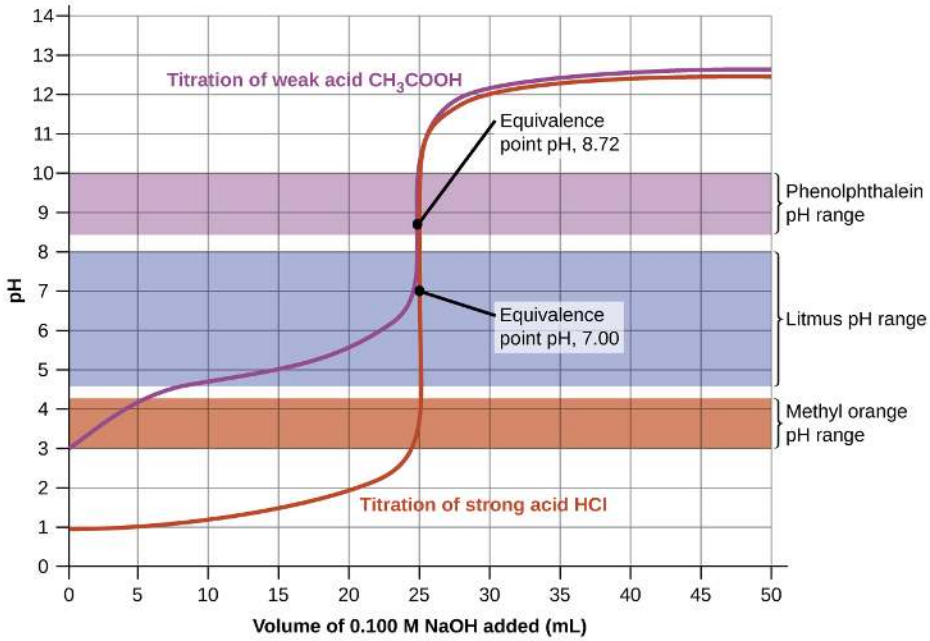


Figure **9.4.2.3**: Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The weak acid titration curve in Figure **9.4.2.3** shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

9.4.2.3: Footnotes

- 1Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
- 2Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

This page titled 9.4.2: Acid-Base Titrations is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **14.7: Acid-Base Titrations** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.5: pH and pOH

Learning Objectives

By the end of this section, you will be able to:

- 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 that 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:

$$pX = -\log X$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$pH = -\log [H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_3O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$pOH = -\log [OH^-]$$

or

$$[OH^-] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_w &= [\mathrm{H_3O^+}]\,[\mathrm{OH^-}] \\ -\log K_w &= -\log \left([\mathrm{H_3O^+}]\,[\mathrm{OH^-}]\right) \\ &= -\log [\mathrm{H_3O^+}] + -\log [\mathrm{OH^-}] \\ pK_w &= pH + pOH \end{aligned} \tag{9.5.1}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = pH + pOH$$

As was demonstrated previously, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log [H_3O^+] = -\log \left(1.0 \times 10^{-7}\right) = 7.00$$

$$pOH = -\log [OH^-] = -\log \left(1.0 \times 10^{-7}\right) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} M and hydroxide ion molarities less than 1.0×10^{-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 1.0×10^{-7} M and hydroxide ion molarities greater than 1.0×10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

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, Exercise **9.5.1** showed the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} M, which corresponds to pH and pOH values of:

$$pH = -\log\left[H_3O^+\right] = -\log\left(4.9 \times 10^{-7}\right) = 6.31$$

$$pOH = -\log\left[OH^-\right] = -\log\left(4.9 \times 10^{-7}\right) = 6.31$$

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 other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C (Table **9.5.1**).

Table **9.5.1**: 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 **9.5.1**: shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

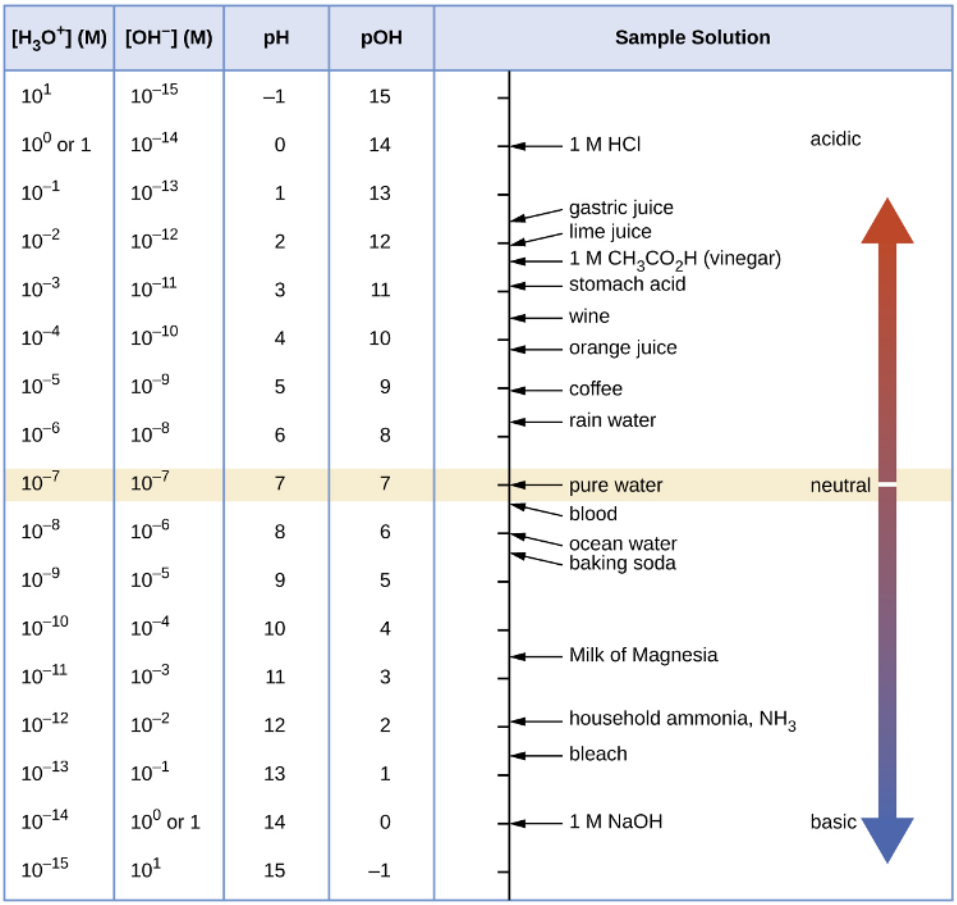


Figure **9.5.1**: The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 9.5.1: 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

$$\begin{aligned} pH &= -\log [H_3O^+] \\ &= -\log \left(1.2 \times 10^{-3}\right) \\ &= -(-2.92) = 2.92 \end{aligned}$$

(The use of logarithms is explained in Appendix B. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Exercise 9.5.1

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 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 9.5.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} pH = -\log [H_3O^+] &= 7.3 \\ \log [H_3O^+] &= -7.3 \\ [H_3O^+] &= 10^{-7.3} \end{aligned}$$

or

$$\begin{aligned} [H_3O^+] &= \text{antilog of } -7.3 \\ &= 5 \times 10^{-8} M \end{aligned}$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 9.5.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 *M*

How Sciences Interconnect: Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)$$
$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

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:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates 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 9.5.2). 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.

For further information on acid rain, visit this website hosted by the US Environmental Protection Agency.



(a) (b)

Figure 9.5.2: (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 ✔ 9.5.3: Calculation of pOH

What are the pOH and the \(\text{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 $[OH^-] = 0.0125\ M$:

$$\text{pOH} = -\log[OH^-] = -\log 0.0125$$
$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$
$$pH = 14.00 - pOH$$
$$= 14.00 - 1.903 = 12.10$$

? Exercise 9.5.3

The hydronium ion concentration of vinegar is approximately 4×10^{-3} M. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6, pH = 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 9.5.3).



(a) (b)

Figure 9.5.3: (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 9.5.4). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.



(a) (b)

Figure 9.5.4: (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

This page titled 9.5: pH and pOH is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **14.2: pH and pOH** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

9.6: Exercises (Equilibrium)

1.

What does it mean to describe a reaction as “reversible”?

2.

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

3.

If a reaction is reversible, when can it be said to have reached equilibrium?

4.

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

5.

If the concentrations of products and reactants are equal, is the system at equilibrium?

6.

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

7.

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown in Figure 13.4.

8.

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

9.

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

10.

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

11.

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

12.

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

13.

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

14.

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

15.

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(d) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$

(e) $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

(f) $Br_2(g) \rightleftharpoons 2Br(g)$

(g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

(h) $CuSO_4{\cdot}5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

16.

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(d) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

(e) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(f) $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$

(g) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$

(h) $S_8(g) \rightleftharpoons 8S(g)$

17.

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17; [NH_3] = 0.20\ M, [N_2] = 1.00\ M, [H_2] = 1.00\ M$
(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4; NH_3 = 3.0\ atm, N_2 = 2.0\ atm, H_2 = 1.0\ atm$
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230; [SO_3] = 0.00\ M, [SO_2] = 1.00\ M, [O_2] = 1.00\ M$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5; SO_3 = 1.00\ atm, SO_2 = 1.00\ atm, O_2 = 1.00\ atm$
(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4; [NO] = 1.00\ M, [Cl_2] = 1.00\ M, [NOCl] = 0\ M$
(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050; NO = 10.0\ atm, N_2 = O_2 = 5\ atm$

18.

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17; [NH_3] = 0.50\ M, [N_2] = 0.15\ M, [H_2] = 0.12\ M$
(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4; NH_3 = 2.00\ atm, N_2 = 10.00\ atm, H_2 = 10.00\ atm$
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230; [SO_3] = 2.00\ M, [SO_2] = 2.00\ M, [O_2] = 2.00\ M$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5\ atm; SO_2 = 1.00\ atm, O_2 = 1.130\ atm, SO_3 = 0\ atm$
(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3; NO = 1.00\ atm, Cl_2 = 1.00\ atm, NOCl = 0\ atm$
(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050; [N_2] = 0.100\ M, [O_2] = 0.200\ M, [NO] = 1.00\ M$

19.

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52 atm

20.

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

$[SO_2Cl_2]$ = 0.12 *M*, $[Cl_2]$ = 0.16 *M* and $[SO_2]$ = 0.050 *M*. K_c for the reaction is 0.078.

21.

Which of the systems described in Exercise 13.15 are homogeneous equilibria? Which are heterogeneous equilibria?

22.

Which of the systems described in Exercise 13.16 are homogeneous equilibria? Which are heterogeneous equilibria?

23.

For which of the reactions in Exercise 13.15 does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

24.

For which of the reactions in Exercise 13.16 does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

25.

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.50$ at 400 °C
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_c = 50.2$ at 448 °C
(c) $Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$ $K_P = 4.08 \times 10^{-25}$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.122$ at 50 °C

26.

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$ $K_c = 4.7 \times 10^{-2}$ at 25 °C
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_P = 48.2$ at 500 °C
(c) $CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g)$ $K_P = 5.09 \times 10^{-44}$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.196$ at 60 °C

27.

What is the value of the equilibrium constant expression for the change Math input error

28.

Write the expression of the reaction quotient for the ionization of HOCN in water.

29.

Write the reaction quotient expression for the ionization of NH_3 in water.

30.

What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (The equilibrium vapor pressure for this substance is 570 torr at 25 °C.)

31.

The following equation represents a reversible decomposition:
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

32.

Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

33.

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

34.

The following reaction occurs when a burner on a gas stove is lit:
$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

35.

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

36.

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

$\mathrm{N_2}(g) + 2\mathrm{H_2}(g) \rightleftharpoons \mathrm{N_2H_4}(g) \qquad \Delta H = 95\ \mathrm{kJ}$

37.

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$\mathrm{P_4}(g) + 6\mathrm{H_2}(g) \rightleftharpoons 4\mathrm{PH_3}(g) \qquad \Delta H = 110.5\ \mathrm{kJ}$

38.

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\mathrm{H_2}(g) \qquad \Delta H = 92\ \mathrm{kJ}$

(b) $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO}(g) \qquad \Delta H = 181\ \mathrm{kJ}$

(c) $2\mathrm{O_3}(g) \rightleftharpoons 3\mathrm{O_2}(g) \qquad \Delta H = -285\ \mathrm{kJ}$

(d) $\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \qquad \Delta H = -176\ \mathrm{kJ}$

39.

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2\mathrm{H_2O}(g) \rightleftharpoons 2\mathrm{H_2}(g) + \mathrm{O_2}(g) \qquad \Delta H = 484\ \mathrm{kJ}$

(b) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g) \qquad \Delta H = -92.2\ \mathrm{kJ}$

(c) $2\mathrm{Br}(g) \rightleftharpoons \mathrm{Br_2}(g) \qquad \Delta H = -224\ \mathrm{kJ}$

(d) $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightleftharpoons 2\mathrm{HI}(g) \qquad \Delta H = 53\ \mathrm{kJ}$

40.

Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$2\mathrm{H_2}(g) + \mathrm{CO}(g) \rightleftharpoons \mathrm{CH_3OH}(g) \qquad \Delta H = -90.2\ \mathrm{kJ}$

(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

41.

Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO}(g) \qquad \Delta H = 181\ \mathrm{kJ}$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

42.

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \qquad \Delta H = 131.30\ \mathrm{kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

43.

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$\mathrm{Fe_2O_3}(s) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{Fe}(s) + 3\mathrm{H_2O}(g) \qquad \Delta H = 98.7\ \mathrm{kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

44.

Ammonia is a weak base that reacts with water according to this equation:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of NH_4Cl

45.

Acetic acid is a weak acid that reacts with water according to this equation:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(aq) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

Will any of the following increase the percent of acetic acid that reacts and produces $\mathrm{CH_3CO_2^-}$ ion?

(a) Addition of HCl

(b) Addition of NaOH

(c) Addition of $NaCH_3CO_2$

46.

Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

$$\Delta H = -65.9\ kJ$$

47.

How can the pressure of water vapor be increased in the following equilibrium?

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta H = 41\ kJ$$

48.

A solution is saturated with silver sulfate and contains excess solid silver sulfate:

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag^+ ions. Explain this observation.

49.

When equal molar amounts of HCl and HOCl are dissolved separately in equal amounts of water, the solution of HCl freezes at a lower temperature. Which compound has the larger equilibrium constant for acid ionization?

(a) HCl

(b) $H^+ + Cl^-$

(c) HOCl

(d) $H^+ + OCl^-$

50.

A reaction is represented by this equation: $A(aq) + 2B(aq) \rightleftharpoons 2C(aq) \qquad K_c = 1 \times 10^3$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations ≤1 *M*, identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

51.

A reaction is represented by this equation: $2W(aq) \rightleftharpoons X(aq) + 2Y(aq) \qquad K_c = 5 \times 10^{-4}$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations of ≤1 *M*, identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

52.

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

53.

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons 3\mathrm{H_2}(g) + \mathrm{CO}(g)$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

54.

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

55.

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 0.0033% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2\mathrm{NO_2}(g) \rightleftharpoons 2\mathrm{NO}(g) + \mathrm{O_2}(g)$$

56.

Calculate the value of the equilibrium constant K_P for the reaction $2\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\mathrm{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

57.

When heated, iodine vapor dissociates according to this equation:

$$\mathrm{I_2}(g) \rightleftharpoons 2\mathrm{I}(g)$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

58.

A sample of ammonium chloride was heated in a closed container.

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g)$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

59.

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the vaporization equilibrium at 60 °C?

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g)$$

60.

Complete the following partial ICE tables.

(a)

	$2\mathrm{SO_3}(g)$	$\rightleftharpoons$	$2\mathrm{SO_2}(g)+$	$\mathrm{O_2}(g)$
change	—		—	$+x$

(b)

	$4NH_3(g)$	$+3O_2(g)$	$\rightleftharpoons$	$2N_2(g)+$	$6H_2O(g)$
change	__	$+x$		__	__

(c)

	$2CH_4(g)$	$\rightleftharpoons$	$C_2H_2(g)+$	$3H_2(g)$
change	__	$+x$		__

(d)

	$CH_4(g)+$	$H_2O(g)$	$\rightleftharpoons$	$CO(g)+$	$3H_2(g)$
change	__	$+x$		__	__

(e)

	$NH_4Cl(s)$	$\rightleftharpoons$	$NH_3(g)+$	$HCl(g)$
change		$+x$	__	

(f)

	$Ni(s)+$	$4CO(g)$	$\rightleftharpoons$	$Ni(CO)_4(g)$
change	$+x$		__	

61.

Complete the following partial ICE tables.

(a)

	$2H_2(g)+$	$O_2(g)$	$\rightleftharpoons$	$2H_2O(g)$
change	__	__		$+x$

(b)

	$CS_2(g)+$	$4H_2(g)$	$\rightleftharpoons$	$CH_4(g)+$	$2H_2S(g)$
change	$+x$	__		__	__

(c)

	$H_2(g)+$	$Cl_2(g)$	$\rightleftharpoons$	$2HCl(g)$
change	$+x$	__		__

(d)

	$2NH_3(g)$	$+2O_2(g)$	$\rightleftharpoons$	$N_2O(g)+$	$3H_2O(g)$
change	__	__		__	$+x$

(e)

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)+$	$H_2S(g)$
change		$+x$	__	

(f)

	$Fe(s)+$	$5CO(g)$	$\rightleftharpoons$	$Fe(CO)_5(g)$
change		__		$+x$

62.

Why are there no changes specified for Ni in Exercise 13.60, part (f)? What property of Ni does change?

63.

Why are there no changes specified for NH_4HS in Exercise 13.61, part (e)? What property of NH_4HS does change?

64.

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\qquad K_c = 0.50$ at 400 °C

Calculate the equilibrium molar concentration of NH_3.

65.

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$$

66.

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_P = 4.7 \times 10^{-2}$$

67.

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad K_P = 1.6 \text{ at } 990\ ^\circ C$$

68.

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \qquad K_c = 4.90 \times 10^2 \text{at } 550\ ^\circ C$$

What concentration of CO remains in an equilibrium mixture with $[CO_2]$ = 0.100 *M*?

69.

Carbon reacts with water vapor at elevated temperatures.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad K_c = 0.2 \text{ at } 1000\ ^\circ C$$

Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with $[H_2O]$ = 0.500 *M* at 1000 °C?

70.

Sodium sulfate 10−hydrate, $Na_2SO_4 \cdot 10H_2O$, dehydrates according to the equation

$$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ ^\circ C$$

What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4 \cdot 10H_2O$ and $NaSO_4$?

71.

Calcium chloride 6−hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

$$CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$ at 25 °C?

72.

A student solved the following problem and found the equilibrium concentrations to be $[SO_2]$ = 0.590 *M*, $[O_2]$ = 0.0450 *M*, and $[SO_3]$ = 0.260 *M*. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3] = 0.500\ M$, $[SO_2] = 0\ M$, and $[O_2] = 0.350\ M$?

73.

A student solved the following problem and found $[N_2O_4] = 0.16\ M$ at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?

$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = 160$

74.

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 1.07 \times 10^{-5}$ in chloroform

(b) Confirm that the change is small enough to be neglected.

75.

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) \qquad K_c = 2.2 \times 10^{-10}$

(b) Confirm that the change is small enough to be neglected.

76.

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g) \qquad K_P = 2.2 \times 10^{-6}$

(b) Confirm that the change is small enough to be neglected.

77.

What are all concentrations after a mixture that contains $[H_2O] = 1.00\ M$ and $[Cl_2O] = 1.00\ M$ comes to equilibrium at 25 °C?

$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_c = 0.0900$

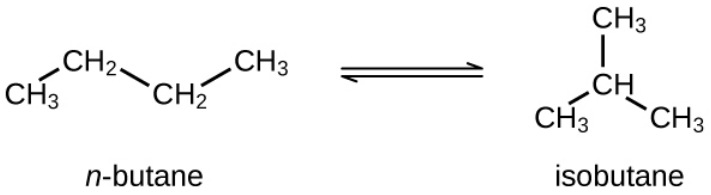
78.

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$

79.

Butane exists as two isomers, *n*−butane and isobutane.



n-butane isobutane

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

80.

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.50 for the decomposition reaction of $CaCO_3$ at that temperature?

$$\mathbf{CaCO_3}(s) \rightleftharpoons \mathbf{CaO}(s) + \mathbf{CO_2}(g)$$

81.

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$\mathbf{H_2}(g) + \mathbf{CO_2}(g) \rightleftharpoons \mathbf{H_2O}(g) + \mathbf{CO}(g)$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

82.

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$\mathbf{N_2}(g) + \mathbf{3H_2}(g) \rightleftharpoons \mathbf{2NH_3}(g)$$

(a) How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

83.

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$\mathbf{CO}(g) + \mathbf{H_2O}(g) \rightleftharpoons \mathbf{CO_2}(g) + \mathbf{H_2}(g)$$

(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

84.

Antimony pentachloride decomposes according to this equation:

$$\mathbf{SbCl_5}(g) \rightleftharpoons \mathbf{SbCl_3}(g) + \mathbf{Cl_2}(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

85.

Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO_2?

(d) If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

86.

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$HbO_2(aq) + H_3O^+(aq) + CO_2(g) \rightleftharpoons CO_2{-}Hb{-}H^+ + O_2(g) + H_2O(l)$$

(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

87.

Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of K_P = 1.91 has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

88.

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*? The equilibrium reaction is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

89.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g) \qquad \Delta G° = -10.88\ kJ$

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g) \qquad \Delta G° = 3.4\ kJ$

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \qquad \Delta G° = -39\ kJ$

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta G° = -141.82\ kJ$

(e) $CS_2(g) \longrightarrow CS_2(l) \qquad \Delta G° = -1.88\ kJ$

90.

Calculate the equilibrium constant at the temperature given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2F_2O(g) \qquad (T = 100\ °C)$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g) \qquad (T = 0.0\ °C)$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$ $(T = 575\ °C)$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ $(T = -10.0\ °C)$

(e) $SnCl_4(l) \longrightarrow SnCl_4(g)$ $(T = 200\ °C)$

91.

Calculate the equilibrium constant at the temperature given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$ $(T = 100\ °C)$

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ $(T = 0.0\ °C)$

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$ $(T = 125\ °C)$

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ $(T = 675\ °C)$

(e) $CS_2(g) \longrightarrow CS_2(l)$ $(T = 90\ °C)$

92.

Consider the following reaction at 298 K:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_P = 0.142$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

93.

Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

94.

Under what conditions is $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ spontaneous?

95.

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

96.

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2H_2S(g) + SO_2(g) \rightleftharpoons \frac{3}{8}S_8(s, \text{rhombic}) + 2H_2O(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

97.

Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

98.

In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

99.

Benzene can be prepared from acetylene. $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

100.

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

101.

Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

$$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$$

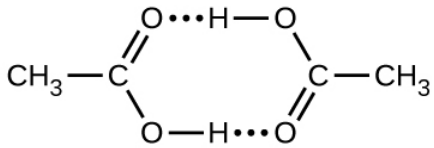
What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

102.

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

$$2CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g)$$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

This page titled 9.6: Exercises (Equilibrium) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

9.6.1: Chapter 13

1.

The reaction can proceed in both the forward and reverse directions.

3.

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to proceed, but at equal rates.

5.

Not necessarily. A system at equilibrium is characterized by *constant* reactant and product concentrations, but the values of the reactant and product concentrations themselves need not be equal.

7.

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

9.

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \frac{1}{[\text{msup}]\text{msup}} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

11.

Since $K_c = \frac{[C_6H_6]}{[C_2H_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

13.

$K_c > 1$

15.

(a) $Q_c = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \frac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) $Q_c = [SO_2]$; (e) $Q_c = \frac{1}{[P_4][O_2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br_2]}$; (g) $Q_c = \frac{[CO_2]}{[CH_4][O_2]^2}$; (h) $Q_c = [H_2O]^5$

17.

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

19.

The system will shift toward the reactants to reach equilibrium.

21.

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

23.

This situation occurs in (a) and (b).

25.

(a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.34 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

27.

$K_P = P_{H_2O} = 0.042$.

29.

$Q_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$

31

The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.

33.

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

34.

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

36.

Add N_2; add H_2; decrease the container volume; heat the mixture.

38.

(a) *T* increase = shift right, *V* decrease = shift left; (b) *T* increase = shift right, *V* = no effect; (c) *T* increase = shift left, *V* decrease = shift left; (d) *T* increase = shift left, *V* decrease = shift right.

40.

(a) $K_c = \frac{[CH_3OH]}{[H_2]^2[CO]}$; (b) $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ increases; (c), $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ decreases; (d), $[H_2]$ increases, [CO] increases, $[CH_3OH]$ increases; (e), $[H_2]$ increases, [CO] increases, $[CH_3OH]$ decreases

42.

(a) $K_c = \frac{[CO][H_2]}{[H_2O]}$; (b) $[H_2O]$ no change, [CO] no change, $[H_2]$ no change; (c) $[H_2O]$ decreases, [CO] decreases, $[H_2]$ decreases; (d) $[H_2O]$ increases, [CO] increases, $[H_2]$ decreases; (f) $[H_2O]$ decreases, [CO] increases, $[H_2]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

44.

Only (b)

46.

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(*s*).

48.

Though the solution is saturated, the dynamic nature of the solubility equilibrium means the opposing processes of solid dissolution and precipitation continue to occur (just at equal rates, meaning the dissolved ion concentrations and the amount of undissolved solid remain constant). The radioactive Ag^+ ions detected in the solution phase come from dissolution of the added solid, and their presence is countered by precipitation of nonradioactive Ag^+.

50.

$K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

52.

$K_c = 6.00 \times 10^{-2}$

54.

$K_c = 0.50$

56.

$K_P = 1.9 \times 10^3$

58.

$K_P = 3.06$

60.

(a) −2*x*, +2*x*; (b) $+\frac{4}{3}x$, $-\frac{2}{3}x$, −2*x*; (c) −2*x*, 3*x*; (d) +*x*, −*x*, −3*x*; (e) +*x*; (f) $-\frac{1}{4}x$.

62.

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

64.

$[NH_3] = 9.1 \times 10^{-2}\ M$

66.

$P_{BrCl} = 4.9 \times 10^{-2}$ atm

68.

$[CO] = 2.04 \times 10^{-4}\ M$

70.

$\mathbf{P_{H_2O} = 3.64 \times 10^{-3}\ atm}$

72.

Calculate *Q* based on the calculated concentrations and see if it is equal to K_c. Because *Q* does equal 4.32, the system must be at equilibrium.

74.

(a) $[NO_2] = 1.17 \times 10^{-3}\ M$
$[N_2O_4] = 0.128\ M$
(b) The assumption that *x* is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the N_2O_4 to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

76.

(a) $[H_2S] = 0.810$ atm
$[H_2] = 0.014$ atm
$[S_2] = 0.0072$ atm
(b) The assumption that 2*x* is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the H_2S to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

78.

507 g

80.

330 g

83.

(a) 0.33 mol.
(b) $[CO]_2 = 0.50\ M$. Added H_2 forms some water as a result of a shift to the left after H_2 is added.

85.

(a) $\mathbf{K_c = \frac{[NH_3]^4[O_2]^7}{[NO_2]^4[H_2O]^6}}$. (b) $[NH_3]$ must increase for Q_c to reach K_c. (c) The increase in system volume would lower the partial pressures of all reactants (including NO_2). (d) $\mathbf{P_{O_2} = 49\ torr}$

87.

$\mathbf{P_{N_2O_3} = 1.90\ atm\ and\ P_{NO} = P_{NO_2} = 1.90\ atm}$

90.

In each of the following, the value of ΔG is not given at the temperature of the reaction. Therefore, we must calculate ΔG from the values $\Delta H°$ and ΔS and then calculate ΔG from the relation $\Delta G = \Delta H° - T\Delta S°$.

(a) $K = 1.07 \times 10^{-13}$;
(b) $K = 2.42 \times 10^{-3}$;
(c) $K = 2.73 \times 10^{4}$;
(d) $K = 0.229$;
(e) $K = 16.1$

92.

The standard free energy change is $\Delta G^\circ_{298} = -RT \ln K = 4.84\ \text{kJ/mol}$. When reactants and products are in their standard states (1 bar or 1 atm), $Q = 1$. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): $Q < 1$, and ΔG_{298} becomes less positive as it approaches zero. At equilibrium, $Q = K$, and $\Delta G = 0$.

94.

The reaction will be spontaneous at temperatures greater than 287 K.

96.

$K = 5.35 \times 10^{15}$
The process is exothermic.

98.

1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

100.

$x = 1.29 \times 10^{-5}\ \text{atm} = P_{O_2}$

102.

−0.16 kJ

This page titled 9.6.1: Chapter 13 is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

9.7: Exercises (Acid-Base)

1.

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

2.

Write equations that show $\mathbf{H_2PO_4^-}$ acting both as an acid and as a base.

3.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) $\mathbf{H_3O^+}$

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) $\mathbf{NH_4^+}$

(f) $\mathbf{HSO_4^-}$

4.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) $\mathbf{PH_4^+}$

(c) H_2S

(d) CH_3CH_2COOH

(e) $\mathbf{H_2PO_4^-}$

(f) HS^-

5.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) H_2O

(b) OH^-

(c) NH_3

(d) CN^-

(e) S^{2-}

(f) $\mathbf{H_2PO_4^-}$

6.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) HS^-

(b) $\mathbf{PO_4^{3-}}$

(c) NH_2^-

(d) C_2H_5OH

(e) O^{2-}

(f) $H_2PO_4^-$

7.

What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) OH^-

(b) H_2O

(c) HCO_3^-

(d) NH_3

(e) HSO_4^-

(f) H_2O_2

(g) HS^-

(h) $H_5N_2^+$

8.

What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H_2S

(b) $H_2PO_4^-$

(c) PH_3

(d) HS^-

(e) HSO_3^-

(f) $H_3O_2^+$

(g) H_4N_2

(h) CH_3OH

9.

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

(b) $CN^- + H_2O \longrightarrow HCN + OH^-$

(c) $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$

(d) $HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$

(e) $O^{2-} + H_2O \longrightarrow 2OH^-$

(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

10.

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $\mathrm{NO_2^- + H_2O \longrightarrow HNO_2 + OH^-}$

(b) $\mathrm{HBr + H_2O \longrightarrow H_3O^+ + Br^-}$

(c) $\mathrm{HS^- + H_2O \longrightarrow H_2S + OH^-}$

(d) $\mathrm{H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O}$

(e) $\mathrm{H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-}$

(f) $\mathrm{[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}}$

(g) $\mathrm{CH_3OH + H^- \longrightarrow CH_3O^- + H_2}$

11.

What are amphiprotic species? Illustrate with suitable equations.

12.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

(a) $\mathrm{H_2O}$

(b) $\mathrm{H_2PO_4^-}$

(c) $\mathrm{S^{2-}}$

(d) $\mathrm{CO_3^{2-}}$

(e) $\mathrm{HSO_4^-}$

13.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a) $\mathrm{NH_3}$

(b) $\mathrm{HPO_4^-}$

(c) $\mathrm{Br^-}$

(d) $\mathrm{NH_4^+}$

(e) $\mathrm{ASO_4^{3-}}$

14.

Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

15.

Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9×10^{-14} at 40 °C.

16.

The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17.

The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

18.

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 *M* HCl

(b) 0.0143 *M* NaOH

(c) 3.0 *M* HNO_3

(d) 0.0031 *M* $Ca(OH)_2$

19.

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 *M* $HClO_4$

(b) 0.21 *M* NaOH

(c) 0.000071 *M* $Ba(OH)_2$

(d) 2.5 *M* KOH

20.

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

21.

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

22.

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 14.2 for useful information.

23.

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

24.

The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25.

The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

26.

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

27.

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

28.

Use this list of important industrial compounds (and Figure 14.8) to answer the following questions regarding: $Ca(OH)_2$, CH_3CO_2H, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.

(b) Identify the compounds that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.

(c) Identify the compounds that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

29.

The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

30.

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

31.

Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

32.

Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

33.

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

34.

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

35.

What is the ionization constant at 25 °C for the weak acid $\mathbf{CH_3NH_3^+}$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

36.

What is the ionization constant at 25 °C for the weak acid $\mathbf{(CH_3)_2NH_2^+}$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?

37.

Which base, CH_3NH_2 or $(CH_3)_2NH$, is the stronger base? Which conjugate acid, $\mathbf{(CH_3)_2NH_2^+}$ or $\mathbf{CH_3NH_3^+}$, is the stronger acid?

38.

Which is the stronger acid, NH_4^+ or HBrO?

39.

Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$?

40.

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a) H_2O or HF

(b) $B(OH)_3$ or $Al(OH)_3$

(c) HSO_3^- or HSO_4^-

(d) NH_3 or H_2S

(e) H_2O or H_2Te

41.

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) HSO_4^- or $HSeO_4^-$

(b) NH_3 or H_2O

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2S or HBr

42.

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI

(b) basicity: H_2O, OH^-, H^-, Cl^-

(c) basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$.)

(d) acidity: HF, H_2O, NH_3, CH_4

43.

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$

(b) basicity: BrO_2^-, ClO_2^-, IO_2^-

(c) acidity: HOCl, HOBr, HOI

(d) acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$

(e) basicity: NH_2^-, HS^-, HTe^-, PH_2^-

(f) basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-

44.

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base?

45.

The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

46.

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

47.

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid or base?

48.

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NH_4Cl

49.

Which of the following will increase the percentage of HF that is converted to the fluoride ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NaF

50.

What is the effect on the concentrations of $\mathbf{NO_2^-}$, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

51.

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

(a) HCl

(b) KF

(c) NaCl

(d) KOH

(e) HF

52.

Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

53.

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}$ *M*;
$[CH_3CO_2^-] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2H] = 9.866 \times 10^{-2}$ *M*;

(b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;

$[HClO] = 2.38 \times 10^{-4}$ *M*;

$[ClO^-] = 0.273$ *M*;

(c) HCO_2H: $[HCO_2H] = 0.524$ *M*;
$[H_3O^+] = 9.8 \times 10^{-3}$ *M*;
$[HCO_2^-] = 9.8 \times 10^{-3}$ *M*;

(d) $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233$ *M*;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;
$[H_3O^+] = 2.3 \times 10^{-3}$ *M*

54.

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;
$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

(b) HNO_2: $[H_3O^+] = 0.011$ *M*;
$[NO_2^-] = 0.0438$ *M*;

$[HNO_2] = 1.07$ *M*;

(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25$ *M*;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}$ *M*;

$[OH^-] = 3.7 \times 10^{-3}$ *M*;

(d) NH_4^+ : $[NH_4^+] = 0.100$ *M*;

$[NH_3] = 7.5 \times 10^{-6}$ *M*;
$[H_3O^+] = 7.5 \times 10^{-6}$ *M*

55.

Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.

56.

Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

57.

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) F^-

(b) NH_4^+

(c) AsO_4^{3-}

(d) $(CH_3)_2NH_2^+$

(e) NO_2^-

(f) $HC_2O_4^-$ (as a base)

58.

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) HTe^- (as a base)

(b) $(CH_3)_3NH^+$

(c) $HAsO_4^{2-}$ (as a base)

(d) HO_2^- (as a base)

(e) $C_6H_5NH_3^+$

(f) HSO_3^- (as a base)

59.

Using the K_a value of 1.4 Math input error

60.

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.

(a) 0.0092 *M* HClO, a weak acid

(b) 0.0784 *M* $C_6H_5NH_2$, a weak base

(c) 0.0810 *M* HCN, a weak acid

(d) 0.11 *M* $(CH_3)_3N$, a weak base

(e) 0.120 *M* $Fe(H_2O)_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

61.

Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-*M* solution of $C_2H_5CO_2H$?

62.

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

63.

The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

64.

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_{b1} = 7 \times 10^{-7}$, $K_{b2} = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

65.

The pH of a 0.23-*M* solution of HF is 1.92. Determine K_a for HF from these data.

66.

The pH of a 0.15-*M* solution of $\mathbf{HSO_4^-}$ is 1.43. Determine K_a for $\mathbf{HSO_4^-}$ from these data.

67.

The pH of a 0.10-*M* solution of caffeine is 11.70. Determine K_b for caffeine from these data:

$$\mathbf{C_8H_{10}N_4O_2}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{C_8H_{10}N_4O_2H^+}(aq) + \mathbf{OH^-}(aq)$$

68.

The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

69.

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $Al(NO_3)_3$

(b) RbI

(c) $KHCO_2$

(d) CH_3NH_3Br

70.

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $FeCl_3$

(b) K_2CO_3

(c) NH_4Br

(d) $KClO_4$

71.

Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

72.

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: $\mathbf{[H_3O^+]}$, $[OH^-]$, $[H_2CO_3]$, $\mathbf{[HCO_3^-]}$, $\mathbf{[CO_3^{2-}]}$? No calculations are needed to answer this question.

73.

Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

74.

Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \qquad K_a = 1.1 \times 10^{-3}$$
$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2{}^{2-}(aq) \qquad K_a = 3.9 \times 10^{-6}$$

75.

Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

76.

The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

77.

Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

78.

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

79.

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

80.

What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

81.

What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq) \qquad K_a = 4.5 \times 10^{-5}$$

82.

What is [OH^-] in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \qquad K_b = 4.4 \times 10^{-4}$$

83.

What is [OH^-] in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

84.

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

(a) HCl

(b) KCH_3CO_2

(c) NaCl

(d) KOH

(e) CH_3CO_2H

85.

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI

(b) NH_3

(c) HI

(d) NaOH

(e) NH_4Cl

86.

What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

87.

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

88.

How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

89.

What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

90.

A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

(a) What is the pH of the solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

91.

A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution

diluted to 0.100 L.

(a) What is the pH of this buffer solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

92.

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

93.

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

94.

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 *M* KOH.

(a) no KOH added

(b) 20 mL of KOH solution added

(c) 39 mL of KOH solution added

(d) 40 mL of KOH solution added

(e) 41 mL of KOH solution added

95.

The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-*M* solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

This page titled 9.7: Exercises (Acid-Base) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

9.7.1: Answers to Selected Exercises

1.

One example for NH_3 as a conjugate acid: $\mathbf{NH_2^- + H^+ \longrightarrow NH_3}$; as a conjugate base: $\mathbf{NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)}$

3.

(a) $\mathbf{H_3}$msupmsup$\mathbf{(aq) \longrightarrow}$ msupmsup$\mathbf{(aq) + H_2O(l)}$; (b) $\mathbf{HCl(aq) \longrightarrow}$ msupmsup$\mathbf{(aq) + Cl^-(aq)}$; (c) $\mathbf{NH_3(aq) \longrightarrow}$ msupmsup$\mathbf{(aq) + NH_2^-(aq)}$; (d) $\mathbf{CH_3CO_2H(aq) \longrightarrow}$ msupmsup$\mathbf{(aq) + CH_3CO_2^-(aq)}$; (e) $\mathbf{NH_4^+(aq) \longrightarrow}$ msupmsup$\mathbf{(aq) + NH_3(aq)}$; (f) $\mathbf{HSO_4^-(aq) \longrightarrow}$ msupmsup$\mathbf{(aq) + SO_4^{2}}$msup$\mathbf{(aq)}$

5.

(a) $\mathbf{H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq)}$; (b) $\mathbf{OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)}$; (c) $\mathbf{NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)}$; (d) $\mathbf{CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)}$; (e) $\mathbf{S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)}$; (f) $\mathbf{H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)}$

7.

(a) H_2O, O^{2-}; (b) H_3O^+, OH^-; (c) H_2CO_3, $\mathbf{CO_3^{2-}}$; (d) $\mathbf{NH_4^+}$, $\mathbf{NH_2^-}$; (e) H_2SO_4, $\mathbf{SO_4^{2-}}$; (f) $\mathbf{H_3O_2^+}$, $\mathbf{HO_2^-}$; (g) H_2S; S^{2-}; (h) $\mathbf{H_6N_2^{2+}}$, H_4N_2

9.

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. (a) HNO_3(BA), H_2O(BB), H_3O^+(CA), $\mathbf{NO_3^-(CB)}$; (b) CN^-(BB), H_2O(BA), HCN(CA), OH^-(CB); (c) H_2SO_4(BA), Cl^-(BB), HCl(CA), $\mathbf{HSO_4^-(CB)}$; (d) $\mathbf{HSO_4^-(BA)}$, OH^-(BB), $\mathbf{SO_4^{2-}}$(CB), H_2O(CA); (e) O^{2-}(BB), H_2O(BA) OH^-(CB and CA); (f) $[Cu(H_2O)_3(OH)]^+$ (BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); (g) H_2S(BA), $\mathbf{NH_2^-(BB)}$, HS^-(CB), NH_3(CA)

11.

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O. As an acid: $\mathbf{H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$. As a base: $\mathbf{H_2O(aq) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)}$

13.

amphiprotic: (a) $\mathbf{NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O}$, $\mathbf{NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH}$; (b) $\mathbf{HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O}$, $\mathbf{HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-}$; not amphiprotic: (c) Br^-; (d) $\mathbf{NH_4^+}$; (e) $\mathbf{AsO_4^{3-}}$

15.

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O^+] = [OH^-] = (2.910 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$.

17.

$x = 3.051 \times 10^{-7}\ M = [H_3O^+] = [OH^-]$; pH = $-\log 3.051 \times 10^{-7} = -(-6.5156) = 6.5156$; pOH = pH = 6.5156

19.

(a) pH = 3.587; pOH = 10.413; (b) pOH = 0.68; pH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pOH = −0.40; pH = 14.4

21.

$[H_3O^+] = 3.0 \times 10^{-7}\ M$; $[OH^-] = 3.3 \times 10^{-8}\ M$

23.

$[H_3O^+] = 1 \times 10^{-2}\ M$; $[OH^-] = 1 \times 10^{-12}\ M$

25.

$[OH^-] = 3.1 \times 10^{-12}\ M$

27.

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

29.

$[H_2O] > [CH_3CO_2H] > \mathbf{[H_3O^+]} \approx \mathbf{[CH_3CO_2^-]} > [OH^-]$

31.

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

33.

$$\underset{\text{BB}}{Mg(OH)_2(s)} + \underset{\text{BA}}{2HCl(aq)} \longrightarrow Mg^{2+}(aq) + \underset{\text{CB}}{2Cl^-(aq)} + \underset{\text{CA}}{2H_2O(l)}$$

35.

$K_a = 2.3 \times 10^-$

37.

The stronger base or stronger acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3^+$.

39.

triethylamine

41.

(a) HSO_4^-; higher electronegativity of the central ion. (b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI; PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI. (d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

43.

(a) $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner. (b) $ClO_2^- < BrO_2^- < IO_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (c) HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three. (d) $HOCl < HOClO < HOClO_2 < HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases). (e) $HTe^- < HS^- << PH_2^- < NH_2^-$; PH_2^- and NH_2^- are anions of weak bases, so they act as strong bases toward H^+. HTe^- and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion. (f) $BrO_4^- < BrO_3^- < BrO_2^- < BrO^-$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

45.

$$[H_2O] > [C_6H_4OH(CO_2H)] > [H^+]\,0 > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]$$

47.

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

48.

(b) The addition of HCl

50.

(a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of NO_2^- ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of OH^- ions. (c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the

concentration of NO_2^- ions and decreasing the concentrations of HNO_2. (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

52.

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

54.

(a) $K_b = 1.8 \times 10^{-5}$; (b) $K_a = 4.5 \times 10^{-4}$; (c) $K_b = 6.4 \times 10^{-5}$; (d) $K_a = 5.6 \times 10^{-10}$

56.

$K_a = 1.2 \times 10^{-2}$

58.

(a) $K_b = 4.3 \times 10^{-12}$ (b) $K_a = 1.6 \times 10^{10}$ (c) $K_b = 5.9 \times 10^{8}$ (d) $K_b = 4.2 \times 10^{-3}$ (e) $K_b = 2.3 \times 10^{5}$ (f) $K_b = 6.3 \times 10^{-13}$

60.

(a) $\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092-x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$

Solving for *x* gives 1.63×10^{-5} *M*. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO^-] = 1.6 \times 10^{-5}$ *M*

$[HClO^-] = 0.0092$ *M*

$[OH^-] = 6.1 \times 10^{-10}$ *M*;

(b) $\frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784-x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$

Solving for *x* gives 5.81×10^{-6} *M*. This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[C_6H_5NH_3^+] = [OH^-] = 5.8 \times 10^{-6}$ *M*

$[C_6H_5NH_2] = 0.0784$ *M*

$[H_3O^+] = 1.7\times 10^{-9}$ *M*;

(c) $\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810-x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$

Solving for *x* gives 6.30×10^{-6} *M*. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [CN^-] = 6.3 \times 10^{-6}$ *M*

$[HCN] = 0.0810$ *M*

$[OH^-] = 1.6 \times 10^{-9}$ *M*;

(d) $\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11-x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$

Solving for *x* gives 2.63×10^{-3} *M*. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[(CH_3)_3NH^+] = [OH^-] = 2.6 \times 10^{-3}$ *M*

$[(CH_3)_3N] = 0.11$ *M*

$[H_3O^+] = 3.8 \times 10^{-12}$ *M*;

(e) $\frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6^{2+}]} = \frac{(x)(x)}{(0.120-x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$

Solving for *x* gives 1.39×10^{-4} *M*. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}$ *M*

$[Fe(H_2O)_6^{2+}] = 0.120$ *M*

$[OH^-] = 7.2 \times 10^{-11}$ *M*

62.

pH = 2.41

64.

$[C_{10}H_{14}N_2] = 0.049\ M$; $[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}\ M$; $[\mathbf{C_{10}H_{14}N_2H_2^{2+}}] = 1.4 \times 10^{-11}\ M$; $[OH^-] = 1.9 \times 10^{-4}\ M$; $[H_3O^+] = 5.3 \times 10^{-11}\ M$

66.

$\mathbf{K_a = 1.2 \times 10^{-2}}$

68.

$\mathbf{K_b = 1.77 \times 10^{-5}}$

70.

(a) acidic; (b) basic; (c) acidic; (d) neutral

72.

$[H_3O^+]$ and $[\mathbf{HCO_3^-}]$ are practically equal

74.

$[C_6H_4(CO_2H)_2]$ $7.2 \times 10^{-3}\ M$, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ $2.8 \times 10^{-3}\ M$, $[\mathbf{C_6H_4(CO_2)_2^{2-}}]$ $3.9 \times 10^{-6}\ M$, $[OH^-]$ $3.6 \times 10^{-12}\ M$

76.

(a) $\mathbf{K_{a2} = 1.5 \times 10^{-11}}$;

(b) $\mathbf{K_b = 4.3 \times 10^{-12}}$;

(c) $\frac{[Te^{2-}][H_3O^+]}{[HTe^-]} = \frac{(x)(0.0141+x)}{(0.0141-x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.5 \times 10^{-11}$

Solving for x gives $1.5 \times 10^{-11}\ M$. Therefore, compared with 0.014 M, this value is negligible (1.1×10^{-7}%).

78.

Excess H_3O^+ is removed primarily by the reaction: $\mathbf{H_3O^+(aq) + H_2PO_4^-(aq) \longrightarrow H_3PO_4(aq) + H_2O(l)}$

Excess base is removed by the reaction: $\mathbf{OH^-(aq) + H_3PO_4(aq) \longrightarrow H_2PO_4^-(aq) + H_2O(l)}$

80.

$[H_3O^+] = 1.5 \times 10^{-4}\ M$

82.

$[OH^-] = 4.2 \times 10^{-4}\ M$

84.

(a) The added HCl will increase the concentration of H_3O^+ slightly, which will react with $\mathbf{CH_3CO_2^-}$ and produce CH_3CO_2H in the process. Thus, $[\mathbf{CH_3CO_2^-}]$ decreases and $[CH_3CO_2H]$ increases. (b) The added KCH_3CO_2 will increase the concentration of $[\mathbf{CH_3CO_2^-}]$ which will react with H_3O^+ and produce CH_3CO_2 H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases. (c) The added NaCl will have no effect on the concentration of the ions. (d) The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $[\mathbf{CH_3CO_2^-}]$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[\mathbf{CH_3CO_2^-}]$ increases. (e) The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $[\mathbf{CH_3CO_2^-}]$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[\mathbf{CH_3CO_2^-}]$ increases.

86.

pH = 8.95

88.

37 g (0.27 mol)

90.

(a) pH = 5.222; (b) The solution is acidic. (c) pH = 5.220

92.

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

94.

(a) pH = 2.50; (b) pH = 4.01; (c) pH = 5.60; (d) pH = 8.35; (e) pH = 11.08

This page titled 9.7.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

CHAPTER OVERVIEW

10: Thermochemistry and Thermodynamics

10.1: Energy Basics
10.2: Calorimetry
10.3: Enthalpy
10.4: Thermodynamics
10.4.1: Spontaneity
10.4.1.1: Entropy
10.4.1.2: The Second and Third Laws of Thermodynamics
10.4.2: New Page
10.5: Free Energy
10.6: Exercises (Thermochemistry)
10.6.1: Answers to Selected Exercises
10.7: Exercises (Thermodynamics)
10.7.1: Answers to Selected Exercises

This page titled 10: Thermochemistry and Thermodynamics is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

10.1: Energy Basics

Learning Objectives

By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure **10.1.1**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a) (b) (c)

Figure **10.1.1**: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

10.1.1: Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against

the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure **10.1.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **10.1.2**: (a) Water at a higher elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry.

10.1.2: Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is "cold" (Figure **10.1.3**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

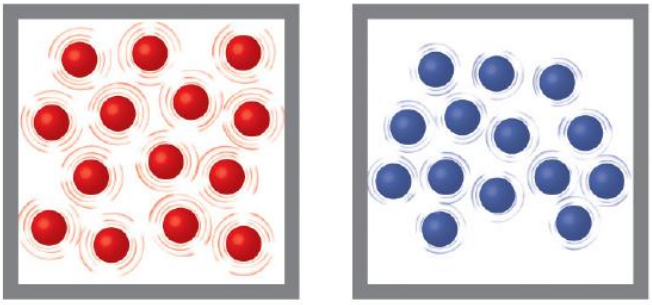


Figure **10.1.3**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Link to Learning

Click on this interactive simulation to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure **10.1.4**. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

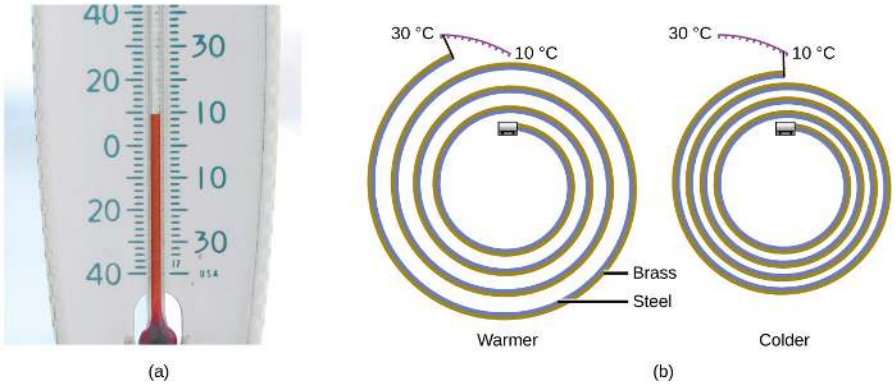


Figure **10.1.4**: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

Link to Learning

The following demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure **10.1.5**).

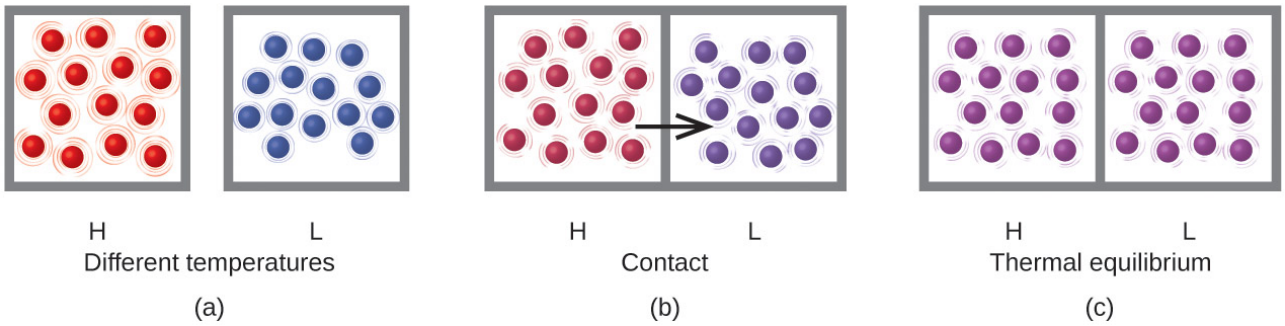


Figure **10.1.5**: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature and their molecules have the same average kinetic energy.

Link to Learning

Click on the PhET simulation to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure **10.1.6**). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure **10.1.6**: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons)

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

$$C_{\text{small pan}} = \frac{18,140J}{50.0°C} = 363J/°C$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700J}{50.0°C} = 1814J/°C$$

The specific heat capacity (*c*) of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140J}{(808g)\,(50.0°C)} = 0.449J/g°C$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700J}{(4040g)\,(50.0°C)} = 0.449J/g°C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure **10.1.7**).



Figure **10.1.7**: Because of its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Water has a relatively high specific heat (about 4.2 J/g °C for the liquid and 2.09 J/g °C for the solid); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this

variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table **10.1.1**.

Table **10.1.1**: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (*state*)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q &= (\text{ specific heat }) \times (\text{ mass of substance }) \times (\text{ temperature change }) \\ &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned} \tag{10.1.1}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

✔ Example 10.1.1: Measuring Heat

A flask containing 8.0 10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0×10^2 g)

- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0×10^2 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 10.1.1:

$$\begin{aligned} q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= \left(4.184 J/\frac{g}{\circ}°C\right) \times (8.0 \times 10^2 g) \times (85 - 21)°C \\ &= (4.184 J/g°C) \times (8.0 \times 10^2 g) \times (64)°C \\ &= 210,000 J \left(= 2.1 \times 10^2 kJ\right) \end{aligned} \tag{10.1.2}$$

Because the temperature increased, the water absorbed heat and q is positive.

? Exercise 10.1.1

How much heat, in joules, must be added to a 502 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Answer

$5.07\ 10^4$ J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

✓ Example 10.1.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship in Equation 10.1.1:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6640 J = c \times (348 g) \times (43.6 - 22.4)°C$$

Solving:

$$c = \frac{6640 J}{(348 g) \times (21.2°C)} = 0.900 J/g°C$$

Comparing this value with the values in Table 10.1.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 10.1.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

c = 0.451 J/g °C; the metal is likely to be iron

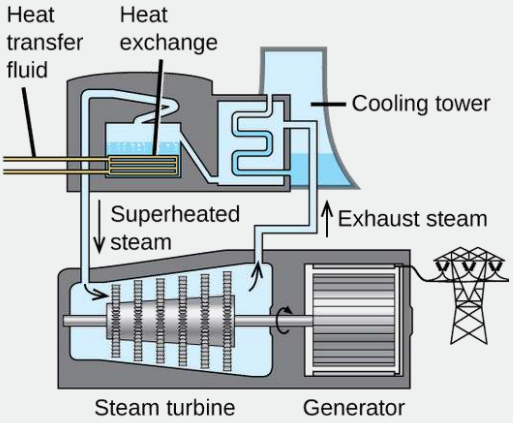
Chemistry in Everyday Life: Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure **10.1.8**). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.



(a)



(b)

Figure **10.1.8**: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure **10.1.9**). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a)



(b)

Figure **10.1.9**: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

This page titled 10.1: Energy Basics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **5.1: Energy Basics** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.2: Calorimetry

Learning Objectives

By the end of this section, you will be able to:

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (all other matter, including components of the measurement apparatus, that serve to either provide heat to the system or absorb heat from the system).

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 10.2.1). 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.

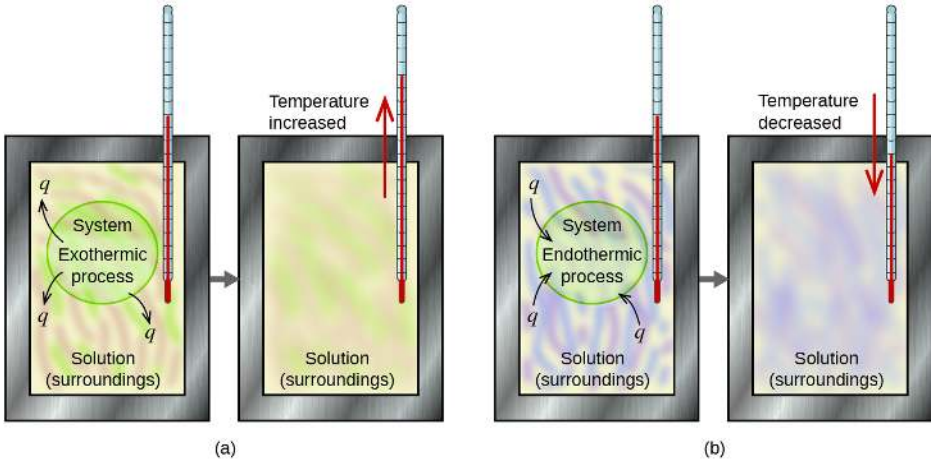


Figure 10.2.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Calorimetry measurements are important in understanding the heat transferred in reactions involving everything from microscopic proteins to massive machines. During her time at the National Bureau of Standards, research chemist Reatha Clark King performed calorimetric experiments to understand the precise heats of various flourine compounds. Her work was important to NASA in their quest for better rocket fuels.

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment, which effectively limits the “surroundings” to the nonsystem components with the calorimeter (and the calorimeter itself). 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 10.2.2). These easy-to-use “coffee cup” calorimeters allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

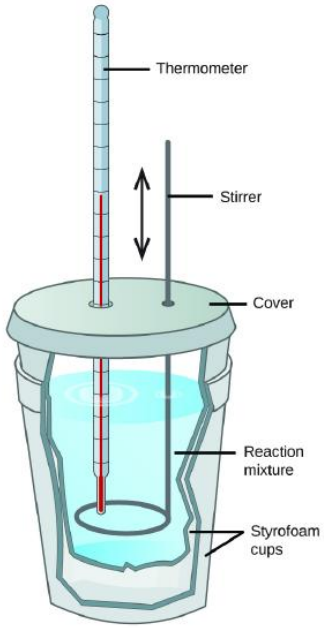


Figure **10.2.2**: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

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 **10.2.3**).

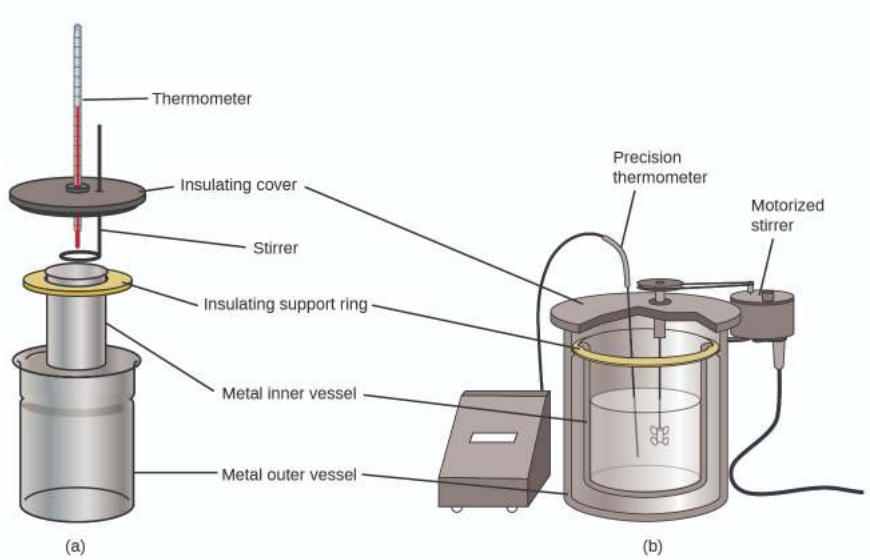


Figure **10.2.3**: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before discussing the calorimetry of chemical reactions, consider a simpler 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 **10.2.4**). 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 its external environment. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance }M} + q_{\text{substance }W} = 0$$

This relationship can be rearranged to 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 therefore 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.

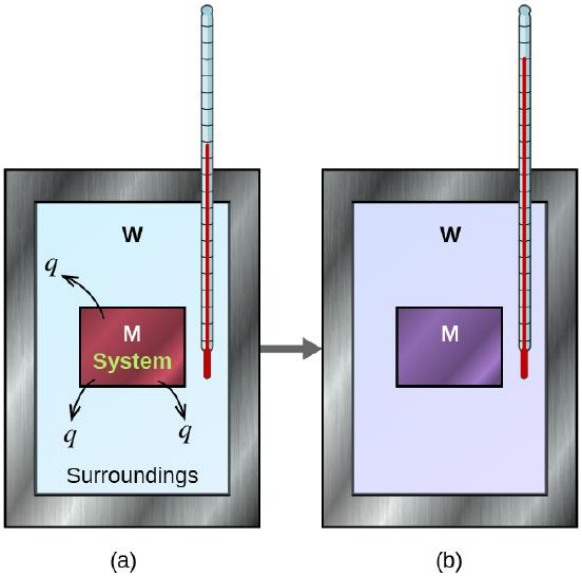


Figure **10.2.4**: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 10.2.1: Heat Transfer between Substances at Different Temperatures

A 360.0-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 was 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 5.1), 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 outside environment, then *heat given off by rebar* = −*heat taken in by water*, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{f,\text{ rebar}} - T_{i,\text{ rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{f,\text{water}} - T_{i,\text{ water}})$$

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:

$$(0.449 J/g^{\circ}C)\,(360.0 g)\,(42.7^{\circ}C - T_{i,\text{ rebar}}) = -(4.184 J/g^{\circ}C)\,(425 g)\,(42.7^{\circ}C - 24.0^{\circ}C)$$

$$T_{i,\text{ rebar}} = \frac{(4.184 J/g^{\circ}C)\,(425 g)\,(42.7^{\circ}C - 24.0^{\circ}C)}{(0.449 J/g^{\circ}C)\,(360.0 g)} + 42.7^{\circ}C$$

Solving this gives $T_{i,\text{ rebar}}$ = 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 10.2.1A

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 10.2.1B

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 10.2.2: 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* = −*heat taken in by water*, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{f,\text{ metal}} - T_{i,\text{ metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{f,\text{water}} - T_{i,\text{ water}})$$

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:

$$(c_{\text{metal}})\,(59.7 g)\,(28.5^{\circ}C - 100.0^{\circ}C) = -(4.18 J/g^{\circ}C)\,(60.0 g)\,(28.5^{\circ}C - 22.0^{\circ}C)$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184 J/g^{\circ}C)\,(60.0 g)\,(6.5^{\circ}C)}{(59.7 g)\,(-71.5^{\circ}C)} = 0.38 J/g^{\circ}C$$

Comparing this with values in Table 5.1, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 10.2.2

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 a 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 outside environment. Because energy is neither created nor destroyed during a chemical reaction, the heat produced or consumed in the reaction (the "system"), \(q_{\text{reaction}}\), plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero:

$$q_{reaction} + q_{solution} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{reaction} = -q_{solution}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example 10.2.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 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?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

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:

$$q_{reaction} = -q_{solution}$$

(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 the outside environment.)

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 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{solution} = (4.184 J/g^{\circ}C)\,(1.0 \times 10^2 g)\,(28.9^{\circ}C - 22.0^{\circ}C) = 2.9 \times 10^3 J$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{reaction} = -q_{solution} = -2.9 \times 10^3 J$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.

Exercise 10.2.3

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 1.3 kJ; 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

Chemistry in Everyday Life: Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 10.2.5). A common reusable hand warmer contains a supersaturated solution of $\mathbf{NaC_2H_3O_2}$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $\mathbf{NaC_2H_3O_2}$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process

$$\mathbf{NaC_2H_3O_2\,(aq) \longrightarrow NaC_2H_3O_2\,(s)}$$

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 $\mathbf{NaC_2H_3O_2}$ redissolves and can be reused.



Figure 10.2.5: 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

$$\mathbf{2\,Fe\,(s) + \tfrac{3}{2}\,O_2\,(g) \longrightarrow Fe_2O_3\,(s)}$$

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.

Link to Learning

This link shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

Example 10.2.4: 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 10.2.6). 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 10.2.6: 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:

$$q_{rxn} = -q_{soln}$$

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:

$$\begin{aligned} q_{rxn} = -q_{soln} &= -(c \times m \times \Delta T)_{soln} \\ &= -\left[(4.184 J/g^{\circ}C) \times (53.2 g) \times (20.3^{\circ}C - 24.9^{\circ}C)\right] \\ &= -\left[(4.184 J/g^{\circ}C) \times (53.2 g) \times (-4.6^{\circ}C)\right] \\ &+ 1.0 \times 10^3 J = +1.0 kJ \end{aligned}$$

The positive sign for *q* indicates that the dissolution is an endothermic process.

Exercise 10.2.4

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.

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 **10.2.7**). 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 absorbed by 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.

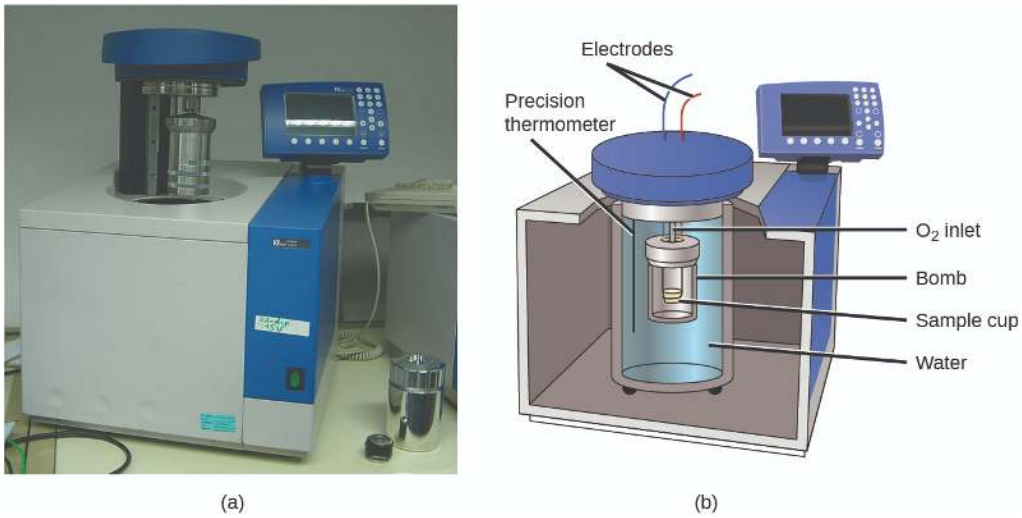


Figure **10.2.7**: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight “bomb,” which is submerged in water and surrounded by insulating materials. (credit a: modification of work by “Harbor1”/Wikimedia commons)

Link to Learning

Click on this link to view how a bomb calorimeter is prepared for action. This site shows calorimetric calculations using sample data.

Example 10.2.5: 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:

$$\begin{aligned} q_{rxn} &= -\left(q_{\text{water}} + q_{\text{bomb}}\right) \\ &= -\left[(4.184 J/g^{\circ}C) \times (775 g) \times (35.6^{\circ}C - 23.8^{\circ}C) + 893 J/^{\circ}C \times (35.6^{\circ}C - 23.8^{\circ}C)\right] \\ &= -(38,300 J + 10,500 J) \\ &= -48,800 J = -48.8 kJ \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

? Exercise 10.2.5

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 benzene sample?

Answer

q_{rx} = –39.0 kJ (the reaction produced 39.0 kJ of heat)

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[2] 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.

For example Carla Prado's team at University of Alberta undertook whole-body calorimetry to understand the energy expenditures of women who had recently given birth. Studies like this help develop better recommendations and regimens for nutrition, exercise, and general wellbeing during this period of significant physiological change. 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.

Chemistry in Everyday Life: 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 **10.2.8**).

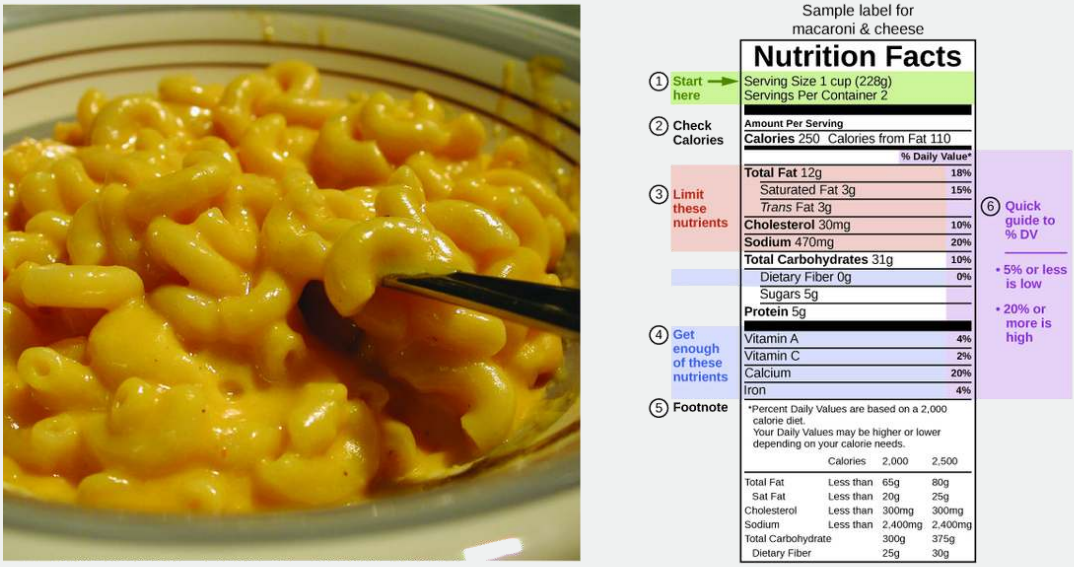


Figure **10.2.8**: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5g \text{ protein } \times 4 \text{ Calories } /g) + (31g \text{ carb } \times 4 \text{ Calories } /g) + (12g \text{ fat } \times 9 \text{ Calories } /g) = 252 \text{ Calories}$$

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.

Link to Learning

Click on this link to access the US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

10.2.1: Footnotes

- 2Francis 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.

This page titled 10.2: Calorimetry is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **5.2: Calorimetry** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.3: Enthalpy

Learning Objectives

By the end of this section, you will be able to:

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the internal energy (U), sometimes symbolized as E.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

as shown in Figure **10.3.1**. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

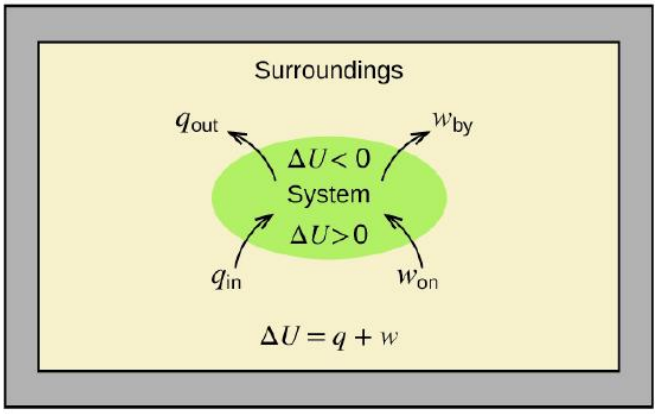


Figure **10.3.1**: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

Link to Learning

This view of an internal combustion engine illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is an example of a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 10.3.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

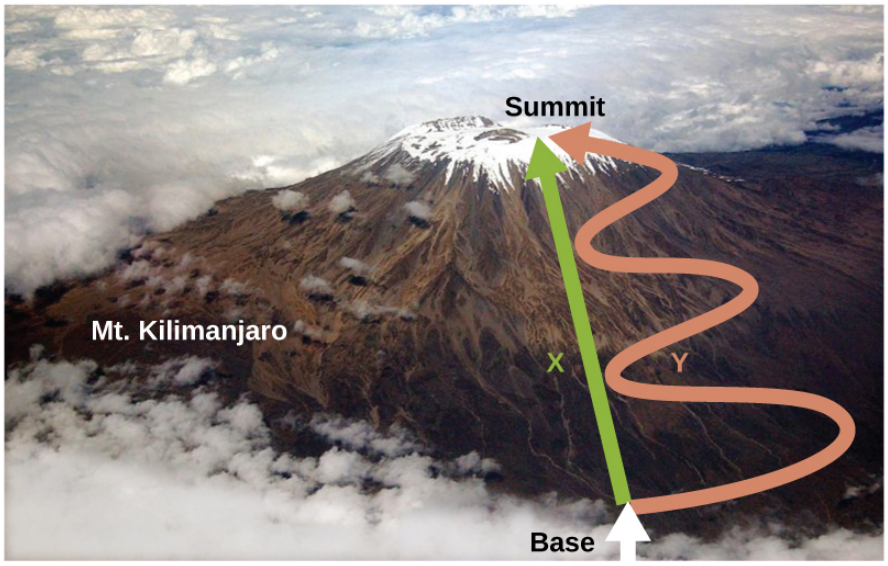


Figure 10.3.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as enthalpy (H) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV$$

Enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will **always** be opposite:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= q_p + w - w \\ &= q_p\end{aligned}$$

where q_p is the **heat of reaction** under conditions of constant pressure.

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 the pressure from remaining constant (it may increase or decrease if the reaction yields increased or decreased amounts of gaseous species). 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 changes for chemical reactions.

The following conventions apply when using ΔH:

- A negative value of an enthalpy change, $\Delta H < 0$, indicates an exothermic reaction; a positive value, $\Delta H > 0$, indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).
- 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:

  $$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)} \quad \Delta H = -286kJ$$

  This equation indicates that when 1 mole of hydrogen gas and 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):

  - two-fold increase in amounts

    $$\mathrm{2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l)} \quad \Delta H = 2 \times (-286kJ) = -572kJ$$

  - two-fold decrease in amounts

    $$\mathrm{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{4}\,O_2\,(g) \longrightarrow \tfrac{1}{2}\,H_2O\,(l)} \quad \Delta H = \frac{1}{2} \times (-286kJ) = -143kJ$$

- The enthalpy change of a reaction depends on the physical states of the reactants and products, so these must be shown. For example, when 1 mole of hydrogen gas and 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.

  $$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} \quad \Delta H = -242kJ$$

Example 10.3.1: Writing Thermochemical Equations

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. Write a balanced thermochemical equation for the reaction of one mole of HCl.

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. The reactants are provided in stoichiometric amounts (same molar ratio as in the balanced equation), and so the amount of acid may be used to calculate a molar enthalpy change. Since ΔH is an extensive property, it is proportional to the amount of acid neutralized:

$$\Delta H = 1 \cancel{\text{ mol HCl}} \times \frac{-2.9 kJ}{0.0500 \cancel{\text{ mol HCl}}} = -58 kJ$$

The thermochemical equation is then

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)} \quad \Delta H = -58 kJ$$

? Exercise 10.3.1

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:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

✓ Example 10.3.2: Writing Thermochemical Equations

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. Write a thermochemical equation for the reaction of one mole of sucrose:

$$\mathrm{C_{12}H_{22}O_{11}\,(aq) + 8\,KClO_3\,(aq) \longrightarrow 12\,CO_2\,(g) + 11\,H_2O\,(l) + 8\,KCl\,(aq)}$$

Solution

Unlike the previous example exercise, this one does not involve the reaction of stoichiometric amounts of reactants, and so the *limiting reactant* must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are

$$(2.67\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{342.3\,\mathrm{g}}\right) = 0.00780\,\mathrm{mol\,C_{12}H_{22}O_{11}}$$

$$(7.19\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{122.5\,\mathrm{g}}\right) = 0.0587\,\mathrm{mol\,KClO}$$

The provided molar ratio of perchlorate-to-sucrose is then

$$\frac{0.0587\,\mathrm{mol\ KClO_3}}{0.00780\,\mathrm{mol\,C_{12}H_{22}O_{11}}} = 7.52$$

The balanced equation indicates 8 mol $KClO_3$ are required for reaction with 1 mol $C_{12}H_{22}O_{11}$. Since the provided amount of $KClO_3$ is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = \frac{-43.7\,\mathrm{kJ}}{0.0587\,\mathrm{molKClO_3}} = \frac{744\,\mathrm{kJ}}{\mathrm{mol\,KClO_3}}$$

Because the equation, as written, represents the reaction of 8 mol $KClO_3$, the enthalpy change is

$$\left(\frac{744\,\text{kJ}}{1\ \cancel{\text{mol KClO}_3}}\right)\left(8\ \cancel{\text{mol KClO}_3}\right) = 5960\,\text{kJ}$$

The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + 8\,\text{KClO}_3 \longrightarrow 12\,\text{CO}_2 + 11\,\text{H}_2\text{O} + 8\,\text{KCl} \quad \Delta H = -5960\,\text{kJ}$$

? Exercise 10.3.1

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $\text{FeCl}_2\,(\text{s})$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $\text{FeCl}_2\,(\text{s})$ is produced?

Answer

ΔH = −338 kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. 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. 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, this temperature will be assumed unless some other temperature is specified. Thus, the symbol 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.)

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.)

10.3.1: Standard Enthalpy of Combustion

Standard enthalpy of combustion 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.

$$\text{C}_2\text{H}_5\text{OH}\,(\text{l}) + 3\,\text{O}_2\,(\text{g}) \longrightarrow 2\,\text{CO}_2 + 3\,\text{H}_2\text{O}\,(\text{l}) \quad \Delta H^\circ = -1366.8\,\text{kJ}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 10.3.1. 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 10.3.1: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH_c° (kJ/mol) at 25 °C
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	−5461

Example 10.3.3: Using Enthalpy of Combustion

As Figure **10.3.3**: 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 **10.3.3**: 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 **10.3.1** gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L C}_8\text{H}_{18}} \times \left(\frac{1000\ \cancel{\text{mL C}_8\text{H}_{18}}}{1\ \cancel{\text{L C}_8\text{H}_{18}}}\right) \times \left(\frac{0.692\ \cancel{\text{g C}_8\text{H}_{18}}}{1\ \cancel{\text{mL C}_8\text{H}_{18}}}\right) \times \left(\frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114\ \cancel{\text{g C}_8\text{H}_{18}}}\right) \times \frac{-5460\ \text{kJ}}{1\ \cancel{\text{mol C}_8\text{H}_{18}}} = -3.31 \times 10^4\ \text{kJ}$$

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:

$$1.00\,\text{L}\,C_8H_{18} \longrightarrow 1.00 \times 10^3\,\text{mL}C_8H_{18}$$
$$1.00 \times 10^3\,\text{mL}\,C_8H_{18} \longrightarrow 692\,\text{g}\,C_8H_{18}$$
$$692\,\text{g}\,C_8H_{18} \longrightarrow 6.07\,\text{mol}\,C_8H_{18}$$
$$6.07\,\text{mol}\,C_8H_{18} \longrightarrow -3.31 \times 10^4 kJ$$

Exercise 10.3.3

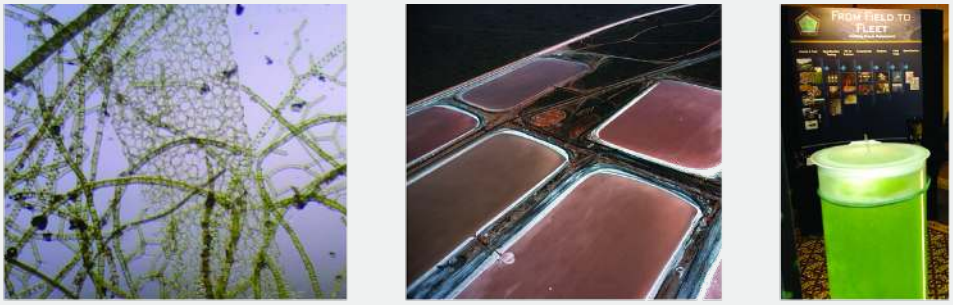
How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25 10^3 kJ

Chemistry in Everyday Life: 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 5.22). 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.



(a) (b) (c)

Figure 5.22 (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 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.[3] 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 **10.3.4**).

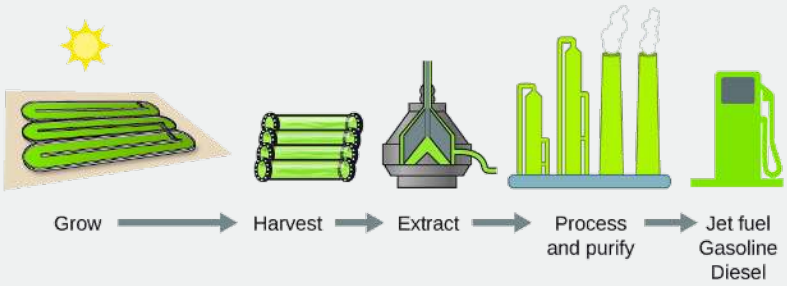


Figure **10.3.4**: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Link to Learning

Click here to learn more about the process of creating algae biofuel.

10.3.2: Standard Enthalpy of Formation

A standard enthalpy of formation 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:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_f^\circ = \Delta H^\circ = -393.5\,kJ}$$

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, $NO_2(g)$, is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\mathrm{\tfrac{1}{2}\,N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H_f^\circ = \Delta H^\circ = +33.2\,kJ}$$

A reaction equation with mole of $\mathrm{N_2}$ and 1 mole of $\mathrm{O_2}$ is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $\mathrm{NO_2(g)}$.

You will find a table of standard enthalpies of formation of many common substances in Thermodynamic Properties Appendix. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of $\mathrm{P_4O_{10}}$) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, $\mathrm{C_2H_2}$). 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 10.3.4: Evaluating an Enthalpy of Formation

Ozone, $\mathrm{O_3(g)}$, forms from oxygen, $\mathrm{O_2(g)}$, 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, of ozone from the following information:

$$\mathrm{3\,O_2(g) \longrightarrow 2\,O_3(g) \quad \Delta H^\circ = +286\,kJ}$$

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, for $\mathrm{O_3(g)}$ is the enthalpy change for the reaction:

$$\mathrm{\tfrac{3}{2}\,O_2(g) \longrightarrow O_3(g)}$$

For the formation of 2 mol of $\mathrm{O_3(g)}$, $\Delta H^\circ = +286\,\mathrm{kJ}$. This ratio, 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 $\mathrm{O_3(g)}$:

$$\mathrm{\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1\,\cancel{mol\,O_3} \times \frac{286\,kJ}{2\,mol\,O_3} = 143\,kJ}$$

Therefore,

$$\mathrm{\Delta H_f^\circ\,[O_3(g)] = +143\,kJ/mol.}$$

? Exercise 10.3.4

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

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H^\circ = -184.6\,kJ$$

✓ Example 10.3.5: Writing Reaction Equations for

Write the heat of formation reaction equations for:

a. $C_2H_5OH(l)$
b. $Ca_3(PO_4)_2(s)$

Solution

Remembering that reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $$2\,C(s, graphite) + 3\,H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_5OH(l)$$

b. $$3\,Ca(s) + \tfrac{1}{2}\,P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

? Exercise 10.3.5

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_5(l)$
b. $Na_2CO_3(s)$

Answer

a. $$4\,C(s, graphite) + 5\,H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_5OC_2H_5(l)$$

b. $$2\,Na(s) + C(s, graphite) + \tfrac{3}{2}\,O_2(g) \longrightarrow Na_2CO_3(s)$$

10.3.3: 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:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ = -394kJ$$

In the two-step process, first carbon monoxide is formed:

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H^\circ = -111 kJ$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ = -283 kJ$$

The equation describing the overall reaction is the sum of these two chemical changes:

step 1	$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$
step 2	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$
sum	$C(s) + \cancel{CO(g)} + O_2(g) \longrightarrow \cancel{CO(g)} + CO_2(g)$

Because the $CO(g)$ produced in Step 1 is consumed in Step 2, the net change is:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.

step 1	$C(s) + \frac{1}{2}O_2(g) \longrightarrow \cancel{CO(g)}$	$\Delta H^\circ = -111\,kJ$
step 2	$\cancel{CO(g)} + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	$\Delta H^\circ = -283\,kJ$
sum	$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H^\circ = -394\,kJ$

The result is shown in Figure 10.3.5. 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 ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

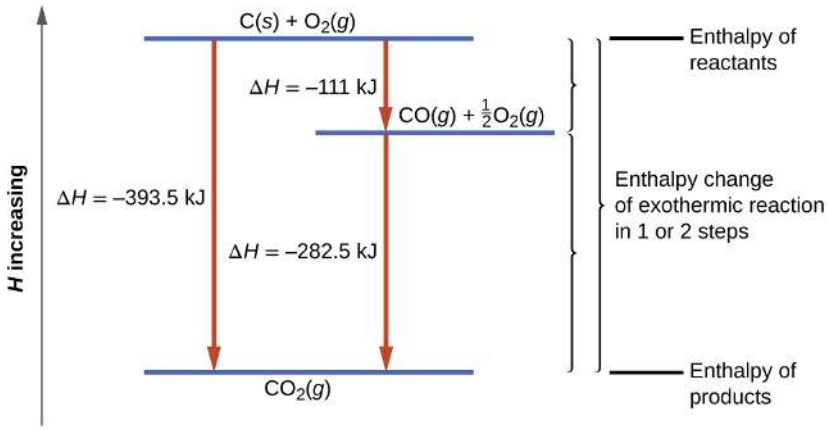


Figure 10.3.5: The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

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:

   $$\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H = +33.2\,kJ$$

   When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

   $$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H = +66.4\,kJ$$

   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 $\Delta H$for the reaction in the reverse direction. For example, given that:

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H = -184.6\,kJ$$

Then, for the "reverse" reaction, the enthalpy change is also "reversed":

Example 10.3.6: Stepwise Calculation of Heat of Formation Using Hess's Law

Determine the enthalpy of formation, of $FeCl_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s) \quad \Delta H^\circ = -341.8\,kJ$$

$$FeCl_2(s) + \tfrac{1}{2}\,Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H^\circ = -57.7\,kJ$$

Solution

We are trying to find the standard enthalpy of formation of $FeCl_3(s)$, which is equal to ΔH° for the reaction:

$$Fe(s) + \tfrac{3}{2}\,Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H_f^\circ = ?$$

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 ΔH values:

step 1	$Fe(s) + Cl_2(g) \longrightarrow \cancel{FeCl2(s)}$	$\Delta H^\circ = -341.8\,kJ$
step 2	$\cancel{FeCl2(s)} + \tfrac{1}{2}\,Cl_2(g) \longrightarrow FeCl_3(s)$	$\Delta H^\circ = -57.7\,kJ$
sum	$Fe(s) + \tfrac{3}{2}\,Cl_2(g) \longrightarrow FeCl_3(s)$	$\Delta H^\circ = -399.5\,kJ$

The enthalpy of formation, ΔH_f° of $FeCl_3(s)$ is −399.5 kJ/mol.

Exercise 10.3.6

Calculate ΔH for the process:

$$N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)$$

from the following information:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H = 180.5\,kJ$$

$$NO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow NO_2(g) \quad \Delta H = -57.06\,kJ$$

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 ΔH) if they are difficult to determine experimentally.

Example 10.3.7: A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

i. $$ClF(g) + F_2(g) \longrightarrow ClF_3(g) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH° for reaction (i):

ii. $$2\,OF_2(g) \longrightarrow O_2(g) + 2\,F_2(g) \quad \Delta H^\circ_{(ii)} = -49.4\,kJ$$

iii. $$2\,ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g) \quad \Delta H^\circ_{(iii)} = +214.0\,kJ$$

iv. $$ClF_3(g) + O_2(g) \longrightarrow \tfrac{1}{2}\,Cl_2O(g) + \tfrac{3}{2}\,OF_2(g) \quad \Delta H^\circ_{(in)} = +236.2\,kJ$$

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 ClF(g) is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$ which means that the ΔH^o change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{1}{2}\,\mathrm{OF_2\,(g)} \quad \Delta H^\circ = \frac{1}{2}(214.0) = +107.0\,\mathrm{kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the ΔH^o changes sign and is halved:

$$\tfrac{1}{2}\,\mathrm{O_2\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{OF_2\,(g)} \quad \Delta H^\circ = +24.7\,\mathrm{kJ}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH^o:

$$\tfrac{1}{2}\,\mathrm{Cl_2O\,(g)} + \tfrac{3}{2}\,\mathrm{OF_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)} + \mathrm{O_2\,(g)} \quad \Delta H^\circ = -236.2kJ$$

Now check to make sure that these reactions add up to the reaction we want:

step 1	$\mathrm{ClF\,(g)} + \cancel{1/2O2(g)} \longrightarrow \cancel{1/2Cl2O(g)} + \cancel{1/2OF2(g)}$	$\Delta H^\circ = +107.0\,\mathrm{kJ}$
step 2	$\cancel{1/2O2(g)} + \mathrm{F_2\,(g)} \longrightarrow \cancel{OF2(g)}$	$\Delta H^\circ = +24.7\,\mathrm{kJ}$
step 3	$\cancel{1/2Cl2O(g)} + \cancel{3/2OF2(g)} \longrightarrow \mathrm{ClF_3\,(g)} + \cancel{O2(g)}$	$\Delta H^\circ = -236.2\,\mathrm{kJ}$
sum	$\mathrm{ClF\,(g)} + \mathrm{F_2\,(g)} \longrightarrow \mathrm{ClF_3\,(g)}$	$\Delta H^\circ = -104.5\,\mathrm{kJ}$

Reactants $\frac{1}{2}\,\mathrm{O_2}$ and $\frac{1}{2}\,\mathrm{O_2}$ cancel out the product $\mathrm{O_2}$; the $\frac{1}{2}\,\mathrm{Cl_2O}$ product cancels $\frac{1}{2}\,\mathrm{Cl_2O}$ reactant and $\frac{3}{2}\,\mathrm{Cl_2O}$ reactant is cancelled by products $\frac{1}{2}\,\mathrm{OF_2}$ and $\mathrm{OF_2}$. This leaves only reactants $\mathrm{ClF\,(g)}$ and $\mathrm{F_2\,(g)}$ and product $\mathrm{ClF_3\,(g)}$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH^o values will give the desired ΔH^o:

$$\Delta H^\circ = (+107.0kJ) + (24.7kJ) + (-236.2kJ) = -104.5\,\mathrm{kJ}$$

? Exercise 10.3.7

Aluminum chloride can be formed from its elements:

i. $$2\,\mathrm{Al\,(s)} + 3\,\mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{AlCl_3\,(s)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction *(i)*:

ii. $$\mathrm{HCl\,(g)} \longrightarrow \mathrm{HCl\,(aq)} \quad \Delta H^\circ_{(ii)} = -74.8\,\mathrm{kJ}$$

iii. $$\mathrm{H_2\,(g)} + \mathrm{Cl_2\,(g)} \longrightarrow 2\,\mathrm{HCl\,(g)} \quad \Delta H^\circ_{(iii)} = -185\,\mathrm{kJ}$$

iv. $$\mathrm{AlCl_3\,(aq)} \longrightarrow \mathrm{AlCl_3\,(s)} \quad \Delta H^\circ_{(iv)} = +323\,\mathrm{kJ}$$

v. $$2\,\mathrm{Al\,(s)} + 6\,\mathrm{HCl\,(aq)} \longrightarrow 2\,\mathrm{AlCl_3\,(aq)} + 3\,\mathrm{H_2\,(g)} \quad \Delta H^\circ_{(v)} = -1049\,\mathrm{kJ}$$

Answer

−1407 kJ

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 ∑ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants })$$

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 10.3.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g) \quad \Delta H^\circ = ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously, and values from the Thermodynamic Properties Appendix:

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants }) \\
&= \left[2\ \cancel{\text{mol HNO}_3\,(aq)} \times \frac{-207.4\,\text{kJ}}{1\ \cancel{\text{mol HNO}_3\,(aq)}} + 1\ \cancel{\text{mol NO}\,(g)} \times \frac{+90.2\,\text{kJ}}{1\ \cancel{\text{mol NO}\,(g)}}\right] \\
&\quad - \left[3\ \cancel{\text{mol NO}_2\,(g)} \times \frac{+33.2\,\text{kJ}}{1\ \cancel{\text{mole NO}_2\,(g)}} + 1\ \cancel{\text{mol H}_2\text{O}\,(l)} \times \frac{-285.8\,\text{kJ}}{1\ \cancel{\text{mol H}_2\text{O}\,(l)}}\right] \\
&= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)] \\
&= -323.03 + 186.23 \\
&= -136.80\,\text{kJ}
\end{aligned}$$

Solution: Supporting Why the General Equation is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\,NO_2\,(g)$ and $H2O(l)$ 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° values for these compounds (from the Thermodynamic Properties Appendix), we have:

$$\begin{aligned}
3\,NO_2\,(g) &\longrightarrow \tfrac{3}{2}\,N_2\,(g) + 3\,O_2\,(g) & \Delta H^\circ_1 &= -99.6\,\text{kJ} \\
H_2O\,(l) &\longrightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) & \Delta H^\circ_2 &= +285.8\,\text{kJ}\ [-1 \times \Delta H^\circ_f\,(H_2O)] \\
H_2\,(g) + N_2\,(g) + 3\,O_2\,(g) &\longrightarrow 2\,HNO_3\,(aq) & \Delta H^\circ_3 &= -414.8\,\text{kJ}\ [2 \times \Delta H^\circ_f\,(HNO_3)] \\
\tfrac{1}{2}\,N_2\,(g) + \tfrac{1}{2}\,O_2\,(g) &\longrightarrow NO\,(g) & \Delta H^\circ_4 &= +90.2\,\text{kJ}\ [1 \times \Delta H^\circ_f(NO)]
\end{aligned}$$

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:

$$\begin{aligned}
\Delta H^\circ_{rxn} &= \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 \\
&= (-99.6\,\text{kJ}) + (+285.8\,\text{kJ}) + (-414.8\,\text{kJ}) + (+90.2\,\text{kJ}) \\
&= -138.4\,\text{kJ}
\end{aligned}$$

So the standard enthalpy change for this reaction is ΔH° = −138.4 kJ.

Note that this result was obtained by:

a. multiplying the of each product by its stoichiometric coefficient and summing those values,
b. multiplying the of each reactant by its stoichiometric coefficient and summing those values, and then
c. subtracting the result found in (2) from the result found in (1).

This is also the procedure in using the general equation, as shown.

? Exercise 10.3.8

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

10.3.4: Footnotes

- 3For more on algal fuel, see http://www.theguardian.com/environme...n-fuel-problem.

This page titled 10.3: Enthalpy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **5.3: Enthalpy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

SECTION OVERVIEW

10.4: Thermodynamics

10.4.1: Spontaneity

10.4.1.1: Entropy

10.4.1.2: The Second and Third Laws of Thermodynamics

10.4.2: New Page

This page titled 10.4: Thermodynamics is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

10.4.1: Spontaneity

Learning Objectives

By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **10.4.1.1**).

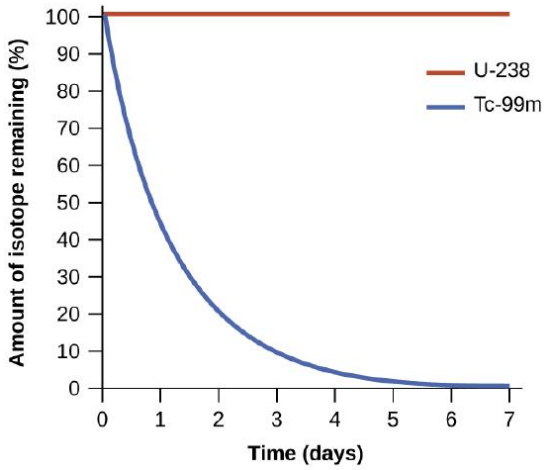


Figure **10.4.1.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure **10.4.1.2**).

$$C(s, \text{diamond}) \longrightarrow C(s, \text{graphite})$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a

process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

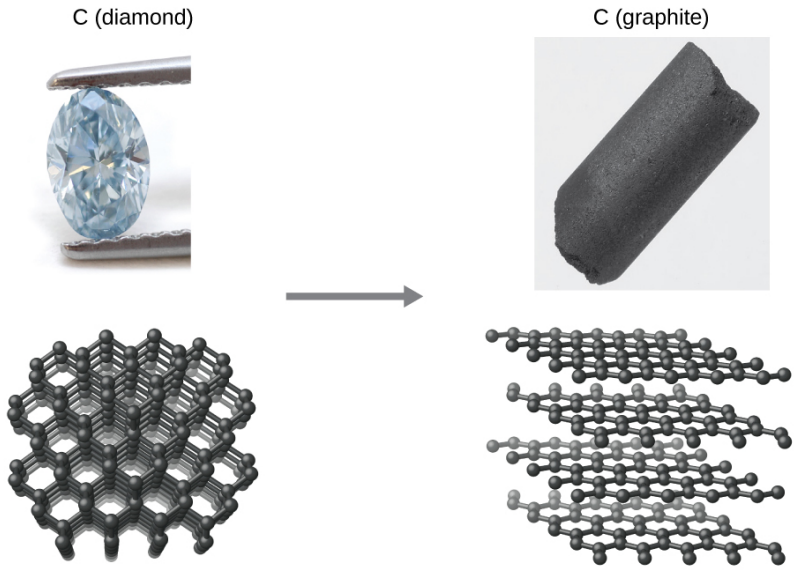


Figure **10.4.1.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

10.4.1.1: Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($\boldsymbol{P = 0}$) (Figure **10.4.1.3**). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

\[w=-P \Delta V=0 \quad \quad (P=0 \text { in a vacuum })|]

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

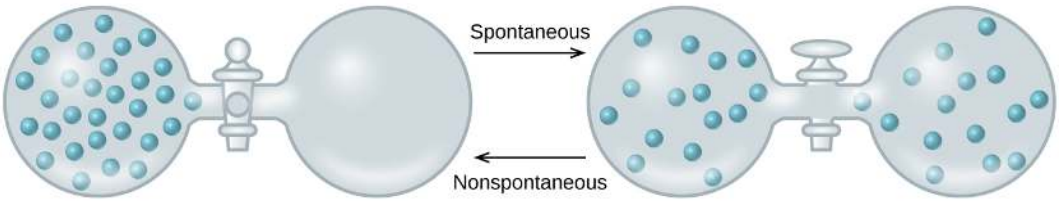


Figure **10.4.1.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure **10.4.1.4**). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y).

This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure **10.4.1.4**: When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 10.4.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure **10.4.1.5**: (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

a. Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.
b. Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.
c. The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Exercise 10.4.1.1

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

This page titled 10.4.1: Spontaneity is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **16.1: Spontaneity** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.4.1.1: Entropy

Learning Objectives

By the end of this section, you will be able to:

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure **10.4.1.1.1**) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

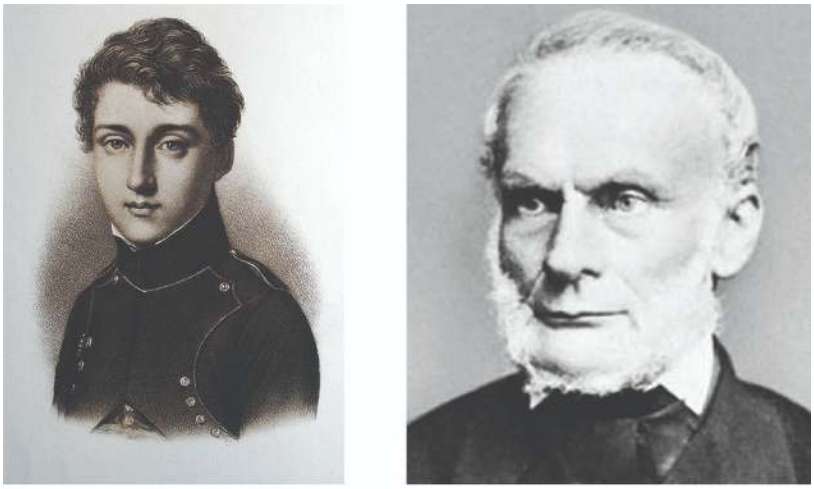


Figure **10.4.1.1.1**: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

10.4.1.1.1: Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (W) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38 10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure **10.4.1.1.2**. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

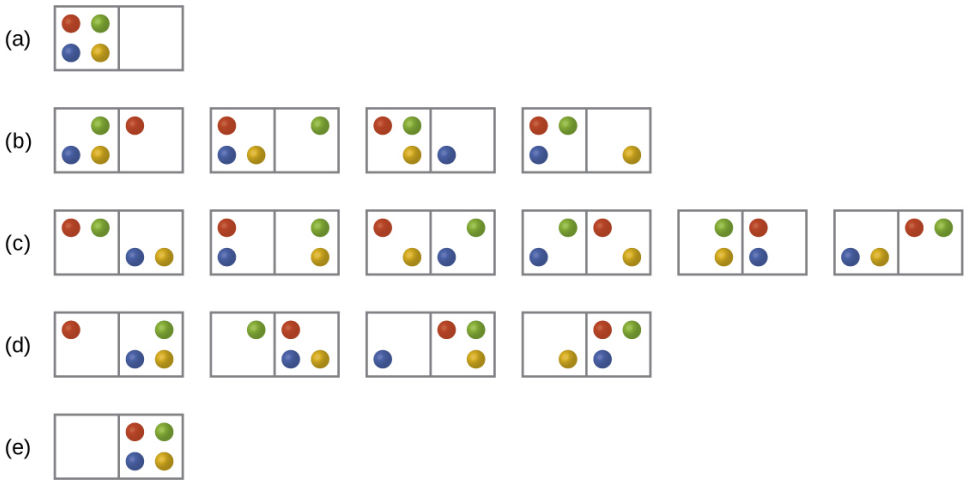


Figure **10.4.1.1.2**: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$ The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of The probability of finding all particles in only one box (either the left box or right box) is then or

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} \text{ or } \frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 16.4) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as "*") in Figure **10.4.1.1.3**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

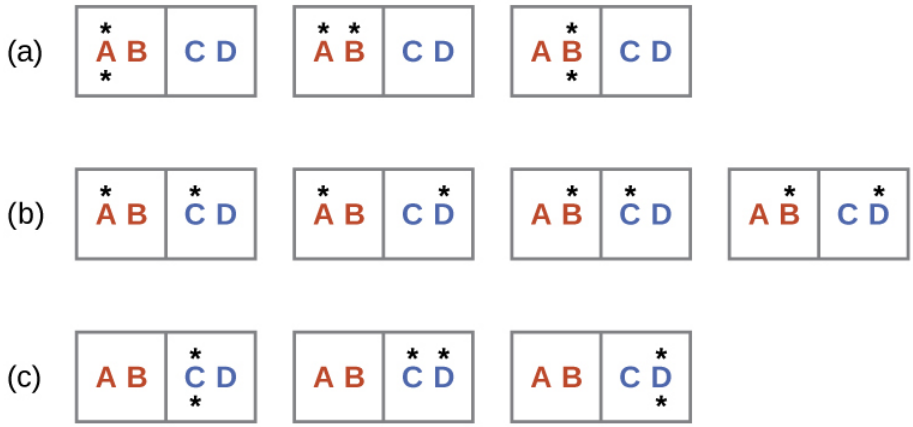
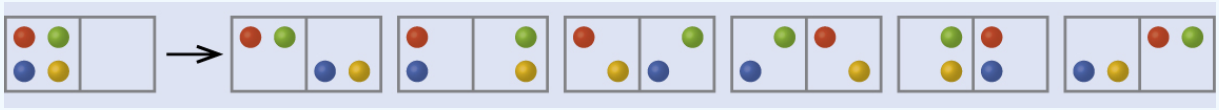


Figure **10.4.1.1.3**: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

✔ Example 10.4.1.1.1: Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23} J/K \times \ln \frac{6}{1} = 2.47 \times 10^{-23} J/K$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

? Exercise 10.4.1.1.1

Consider the system shown in Figure **10.4.1.1.3**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

10.4.1.1.2: Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure **10.4.1.1.4**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

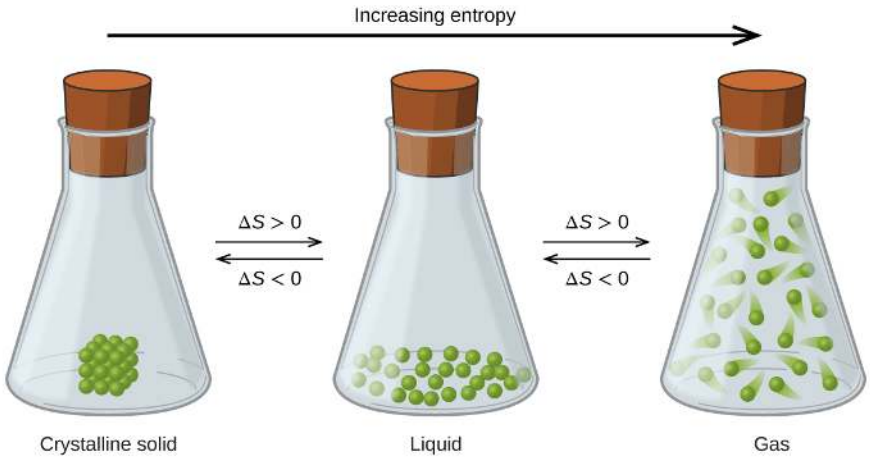


Figure **10.4.1.1.4**: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure **10.4.1.1.5**).

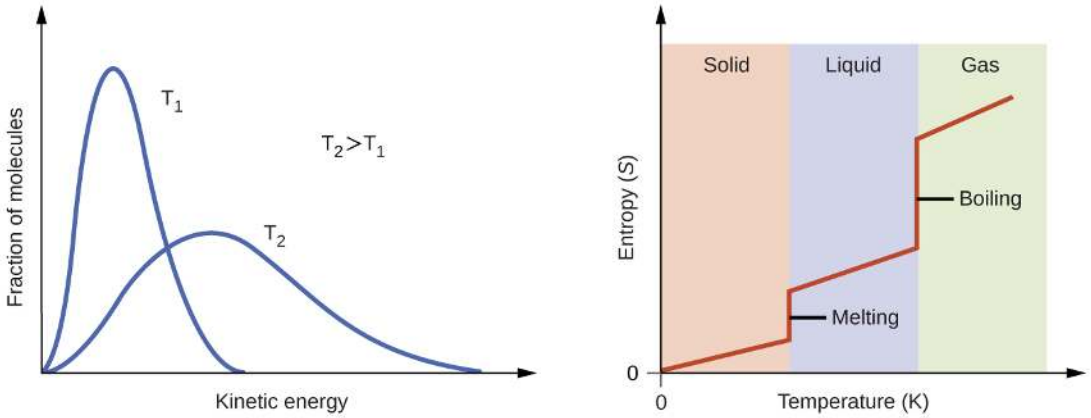


Figure **10.4.1.1.5**: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example **10.4.1.1.2**.

Example 10.4.1.1.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature one mole liquid water at 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. \(C_6 H_6(l)+\frac{15}{2} O_2(g) \longrightarrow 6 CO_2(g)+3 H_2O(l))
d. $NH_3(s) \longrightarrow NH_3(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 10.4.1.1.1

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a. $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3^-(aq)$
b. the freezing of liquid water
c. $CO_2(s) \longrightarrow CO_2(g)$
d. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Answer

(a) Positive; The solid dissolves to give an increase of mobile ions in solution.

(b) Negative; The liquid becomes a more ordered solid.

(c) Positive; The relatively ordered solid becomes a gas.

(d) Positive; There is a net increase in the amount of gaseous species.

This page titled 10.4.1.1: Entropy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **16.2: Entropy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.4.1.2: The Second and Third Laws of Thermodynamics

Learning Objectives

By the end of this section, you will be able to:

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

10.4.1.2.1: The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{q_{rev}}{T_{surr}}$$

   The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

   $$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$
   $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{sys} = \frac{q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{-q_{rev}}{T_{surr}}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

   $$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$
   $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table **10.4.1.2.1**.

Table **10.4.1.2.1**: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	at equilibrium

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example **10.4.1.2.1**.

Example 10.4.1.2.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$H_2O(s) \longrightarrow H_2O(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{263.15 K} = -0.7 J/K\end{aligned}$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \frac{q_{surr}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{283.15 K} = +0.9 J/K\end{aligned}$$

$S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

Exercise 10.4.1.2.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, so $\Delta S_{freezing} = -\Delta S_{melting}$ = −22.1 J/K and q_{surr} = +6.00 kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

10.4.1.2.2: The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies** ($S°$) are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change** ($\Delta S°$) for a reaction may be computed using standard entropies as shown below:

$$\Delta S° = \sum \nu S°(\text{ products }) - \sum \nu S°(\text{ reactants })$$

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD$$

is computed as:

$$= [xS°(C) + yS°(D)] - [mS°(A) + nS°(B)]$$

A partial listing of standard entropies is provided in Table **10.4.1.2.2**, and additional values are provided in Appendix G. The example exercises that follow demonstrate the use of $S°$ values in calculating standard entropy changes for physical and chemical processes.

Table **10.4.1.2.2**: Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	($J\ mol^{-1}\ K^{-1}$)
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
H(*g*)	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(*g*)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 10.4.1.2.2: Determination of $\Delta S°$

Calculate the standard entropy change for the following process:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S° = (1mol)\left(70.0Jmol^{-1}K^{-1}\right) - (1mol)\left(188.8Jmol^{-1}K^{-1}\right) = -118.8J/K$$

The value for $\Delta S°$ is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 10.4.1.2.2

Calculate the standard entropy change for the following process:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

$-120.6\ J\ K^{-1}\ mol^{-1}$

Example 10.4.1.2.3: Determination of $\Delta S°$

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S° = \sum \nu S°(\text{ products }) - \sum \nu S°(\text{ reactants })$$

$$[2mol \times S°(CO_2(g)) + 4mol \times S°(H_2O(l))] - [2mol \times S°(CH_3OH(l)) + 3mol \times S°(O_2(g)]$$

$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6J/K$$

Exercise 10.4.1.2.3

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/K

This page titled 10.4.1.2: The Second and Third Laws of Thermodynamics is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **16.3: The Second and Third Laws of Thermodynamics** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.4.2: New Page

This page titled 10.4.2: New Page is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

10.5: Free Energy

Learning Objectives

By the end of this section, you will be able to:

- Define Gibbs free energy, and describe its relation to spontaneity
- Explain how temperature affects the spontaneity of some processes

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy** (*G*) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the free energy change (ΔG) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table **10.5.1** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table **10.5.1**: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

10.5.1: What's "Free" about ΔG?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S$$

may be interpreted as representing the difference between the energy produced by the process, ΔH, and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, ΔG. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{max}$$

where w_{max} refers to all types of work except expansion (pressure-volume) work.

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., batteries) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done *on* the system to carry out the process.

10.5.2: Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute **standard free energy changes**, ΔG^o, according to the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

It is important to understand that for phase changes, ΔG^o tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG^o tells you the **extent** of a reaction. In other words, ΔG^o for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^o < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^o > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

10.5.3: Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

> **Note**
>
> The numerical value of ΔG^o is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG^o is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH^o and ΔS^o are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is greater than ΔH^o. If the $T\Delta S^o$ term is less than ΔH^o, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures.*
2. **Both ΔH^o and ΔS^o are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is less than ΔH^o. If the $T\Delta S^o$ term's magnitude is greater than ΔH^o, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures.*
3. **ΔH^o is positive and ΔS^o is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG^o will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures.*
4. **ΔH^o is negative and ΔS^o is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures.*

These four scenarios are summarized in Table **10.5.1**

Table **10.5.1**

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When $\Delta G^o < 0$, $K > 1$, and the reaction will be product-favored at equilibrium. When $\Delta G^o > 0$, $K < 1$, and the reaction is reactant-favored at equilibrium. When $\Delta G^o = 0$, $K = 1$, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔG^o can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

This page titled 10.5: Free Energy is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall via source content that was edited to the style and standards of the LibreTexts platform.

- **16.4: Free Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **16.4: Gibbs Energy** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

10.6: Exercises (Thermochemistry)

1.

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

2.

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

3.

Explain the difference between heat capacity and specific heat of a substance.

4.

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 28.4 g of water

(b) 1.00 oz of lead

5.

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

6.

How much heat, in joules and in calories, must be added to a 75.0–g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

7.

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from −23.0 °C to −1.0 °C?

8.

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

9.

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

10.

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in Table 9.1, what is its likely identity?

11.

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in Table 9.1, what is its likely identity?

12.

An aluminum kettle weighs 1.05 kg.

(a) What is the heat capacity of the kettle?

(b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?

(c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

13.

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

14.

A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

15.

Would the amount of heat measured for the reaction in Example 9.5 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

16.

Would the amount of heat absorbed by the dissolution in Example 9.6 appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

17.

Would the amount of heat absorbed by the dissolution in Example 9.6 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

18.

How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

19.

How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

20.

A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two become equal.

(a) What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.

(b) The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.

21.

The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

22.

A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in Figure 9.12. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

23.

If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure 9.12, what is the resulting temperature of the water?

24.

A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure 9.12). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

25.

Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure 9.12) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

26.

When 50.0 g of 0.200 M $NaCl(aq)$ at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as $AgCl(s)$ forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

27.

The addition of 3.15 g of $Ba(OH)_2{\cdot}8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

$$Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(aq) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

28.

The reaction of 50 mL of acid and 50 mL of base described in Example 9.5 increased the temperature of the solution by 6.9 ºC. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 ºC? Explain your answer.

29.

If the 3.21 g of NH_4NO_3 in Example 9.6 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

30.

When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion?

31.

When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

32.

One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter (Figure 9.17), the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000×10^3 pounds).

33.

The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is
9.1 Calories/g?

34.

A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

35.

What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?

36.

A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is
9.1 Calories/g?

37.

A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

38.

Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

39.

Explain how the heat measured in Example 9.5 differs from the enthalpy change for the exothermic reaction described by the following equation:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

40.

Using the data in the check your learning section of Example 9.5, calculate ΔH in kJ/mol of $AgNO_3(aq)$ for the reaction: $\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq)$

41.

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH_4NO_3 under the conditions described in Example 9.6.

42.

Calculate ΔH for the reaction described by the equation. (*Hint*: Use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.)

$$\mathrm{Ba(OH)_2 \cdot 8H_2O}(s) + 2\mathrm{NH_4SCN}(aq) \longrightarrow \mathrm{Ba(SCN)_2}(aq) + 2\mathrm{NH_3}(aq) + 10\mathrm{H_2O}\,(l)$$

43.

Calculate the enthalpy of solution (ΔH for the dissolution) per mole of $CaCl_2$ (refer to Exercise 9.25).

44.

Although the gas used in an oxyacetylene torch (Figure 9.7) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in Table 9.2. Considering the conditions for which the tabulated data are reported, suggest an explanation.

45.

How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

46.

How much heat is produced by combustion of 125 g of methanol under standard state conditions?

47.

How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

48.

What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

49.

When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

50.

How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \longrightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l) \qquad \Delta H° = -58\ \mathrm{kJ}$$

If both solutions are at the same temperature and the specific heat of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

51.

A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

52.

Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)?

The vaporization reactions for SO_2 and CCl_2F_2 are $\mathrm{SO_2}(l) \longrightarrow \mathrm{SO_2}(g)$ and $\mathrm{CCl_2F}\,(l) \longrightarrow \mathrm{CCl_2F_2}(g)$, respectively.

53.

Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

54.

Which of the enthalpies of combustion in Table 9.2 the table are also standard enthalpies of formation?

55.

Does the standard enthalpy of formation of $H_2O(g)$ differ from $\Delta H°$ for the reaction $\mathrm{2H_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2H_2O}\,(g)$?

56.

Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red HgO(s) to Hg(l) and $O_2(g)$ under standard conditions?

57.

How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?

58.

How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form $Fe_2O_3(s)$ at standard state conditions?

59.

The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO\,(g) + 6H_2O\,(l) \qquad \Delta H = -907\,kJ$

$2NO\,(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = -113\,kJ$

$3NO_2 + H_2O\,(l) \longrightarrow 2HNO_3(aq) + NO(g) \qquad \Delta H = -139\,kJ$

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

60.

Both graphite and diamond burn.

$C\,(s,\ \text{diamond}) + O_2(g) \longrightarrow CO_2(g)$

For the conversion of graphite to diamond:

$C\,(s,\ \text{graphite}) \longrightarrow C\,(s,\ \text{diamond}) \qquad \Delta H° = 1.90\,kJ$

Which produces more heat, the combustion of graphite or the combustion of diamond?

61.

From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water: $H_2O\,(l) \longrightarrow H_2O\,(g)$

62.

Which produces more heat?

$Os\,(s) \longrightarrow 2O_2(g) \longrightarrow OsO_4(s)$

or

$Os\,(s) \longrightarrow 2O_2(g) \longrightarrow OsO_4(g)$

for the phase change $OsO_4(s) \longrightarrow OsO_4(g) \qquad \Delta H = 56.4\,kJ$

63.

Calculate $\Delta H°$ for the process

$Sb\,(s) + \frac{5}{2}Cl_2(g) \longrightarrow SbCl_5(s)$

from the following information:

$Sb\,(s) + \frac{3}{2}Cl_2(g) \longrightarrow SbCl_3(s) \qquad \Delta H° = -314\,kJ$

$SbCl_3(s) + Cl_2(g) \longrightarrow SbCl_5(s) \qquad \Delta H° = -80\,kJ$

64.

Calculate $\Delta H°$ for the process $Zn\,(s) + S\,(s) + 2O_2(g) \longrightarrow ZnSO_4(s)$

from the following information:

$Zn(s) + S(s) \longrightarrow ZnS(s) \qquad \Delta H° = -206.0\,kJ$

$ZnS(s) + 2O_2(g) \longrightarrow ZnSO_4(s) \qquad \Delta H° = -776.8\,kJ$

65.

Calculate ΔH for the process $Hg_2Cl_2(s) \longrightarrow 2Hg\,(l) + Cl_2(g)$

from the following information:

$Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s) \qquad \Delta H = -224\,kJ$

$Hg(l) + HgCl_2(s) \longrightarrow Hg_2Cl_2(s) \qquad \Delta H = -41.2\,kJ$

66.

Calculate $\Delta H°$ for the process $Co_3O_4(s) \longrightarrow 3Co(s) + 2O_2(g)$

from the following information:

$Co(s) + \frac{1}{2}O_2(g) \longrightarrow CoO(s) \qquad \Delta H° = -237.9 kJ$

$3CoO(s) + \frac{1}{2}O_2(g) \longrightarrow Co_3O_4(s) \qquad \Delta H° = -177.5 kJ$

67.

Calculate the standard molar enthalpy of formation of NO(g) from the following data:

$N_2(g) + 2O_2 \longrightarrow 2NO_2(g) \qquad \Delta H° = 66.4\ kJ$

$2NO(g) + O_2 \longrightarrow 2NO_2(g) \qquad \Delta H° = -114.1\ kJ$

68.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(b) $Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g)$

(c) $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

69.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $Si(s) + 2F_2(g) \longrightarrow SiF_4(g)$

(b) $2C(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3CO_2H(l)$

(c) $CH_4(g) + N_2(g) \longrightarrow HCN(g) + NH_3(g)$;

(d) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

70.

The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

(a) $2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$

(b) $SnO(s) + CO(g) \longrightarrow Sn(s) + CO_2(g)$

(c) $Cr_2O_3(s) + 3H_2(g) \longrightarrow 2Cr(s) + 3H_2O(l)$

(d) $2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

71.

The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix G, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

$2H_2O_2(l) \longrightarrow 2H_2O(g) + O_2(g)$

72.

Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is −104 kJ/mol.

73.

Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is −126 kJ/mol.

74.

Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

75.

The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, $TiCl_4$, with water vapor in the gas phase: $\mathrm{TiCl_4}(g) + 2\mathrm{H_2O}\,(g) \longrightarrow \mathrm{TiO_2}(s) + 4\mathrm{HCl}\,(g)$.

How much heat is evolved in the production of exactly 1 mole of $TiO_2(s)$ under standard state conditions?

76.

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon: $\mathrm{C}\,(s) + \mathrm{H_2O}\,(g) \longrightarrow \mathrm{CO}\,(g) + \mathrm{H_2}(g)$.

(a) Assuming that coke has the same enthalpy of formation as graphite, calculate $\Delta H°$ for this reaction.

(b) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst: $2\mathrm{H_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{CH_3OH}(g)$.

Under the conditions of the reaction, methanol forms as a gas. Calculate $\Delta H°$ for this reaction and for the condensation of gaseous methanol to liquid methanol.

(c) Calculate the heat of combustion of 1 mole of liquid methanol to $H_2O(g)$ and $CO_2(g)$.

77.

In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2. Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2:
$\mathrm{CaC_2}(s) + 2\mathrm{H_2O}\,(l) \longrightarrow \mathrm{Ca(OH)_2}(s) + \mathrm{C_2H_2}(g)$.
Calculate the standard enthalpy of the reaction. The $\Delta H_f°$ of CaC_2 is −15.14 kcal/mol.

78.

From the data in Table 9.2, determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $CO(g)$, $CH_4(g)$, or $C_2H_2(g)$.

79.

The enthalpy of combustion of hard coal averages −35 kJ/g, that of gasoline, 1.28×10^5 kJ/gal. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

80.

Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.

(a) Write the balanced equation for the combustion of ethanol to $CO_2(g)$ and $H_2O(g)$, and, using the data in Appendix G, calculate the enthalpy of combustion of 1 mole of ethanol.

(b) The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.

(c) Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n–octane, C_8H_{18} ($\Delta H_f^\circ = -208.4\ \text{kJ/mol}$; density = 0.7025 g/mL).

81.

Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6, produces $B_2O_3(s)$ and $H_2O(g)$], methane [CH_4, produces $CO_2(g)$ and $H_2O(g)$], and hydrazine [N_2H_4, produces $N_2(g)$ and $H_2O(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The Math input error

82.

How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?

83.

Ethylene, C_2H_4, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst. $\mathbf{C_2H_4}(g) + \mathbf{H_2O}\,(g) \longrightarrow \mathbf{C_2H_5OH}\,(l)$

Using the data in the table in Appendix G, calculate $\Delta H°$ for the reaction.

84.

The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:

$\mathbf{C_6H_{12}O_6}(s) + \mathbf{6O_2}(g) \longrightarrow \mathbf{6CO_2}(g) + \mathbf{6H_2O}\,(l) \qquad \Delta H = -2816\ \text{kJ}$

The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

(a) How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?

(b) How many Calories can be produced by the metabolism of 1.0 g of glucose?

85.

Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel.

(a) Write a balanced equation for the complete combustion of propane gas.

(b) Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: We will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2.)

(c) The heat of combustion of propane is −2,219.2 kJ/mol. Calculate the heat of formation, ΔH_f° of propane given that ΔH_f° of $H_2O(l)$ = −285.8 kJ/mol and ΔH_f° of $CO_2(g)$ = −393.5 kJ/mol.

(d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

86.

During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

(a) Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.

(b) How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.

(c) What mass of carbon dioxide is produced by combustion of the methane used to heat the house?

(d) What mass of water is produced by combustion of the methane used to heat the house?

(e) What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.

(f) How many kilowatt–hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.

(g) Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

87.

Which bond in each of the following pairs of bonds is the strongest?

(a) C–C or $\mathbf{C=C}$

(b) C–N or $\mathbf{C\equiv N}$

(c)$\mathbf{C\equiv O}$ or $\mathbf{C=O}$

(d) H–F or H–Cl

(e) C–H or O–H

(f) C–N or C–O

88.

Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $\mathbf{H_2}(g) + \mathbf{Br_2}(g) \longrightarrow \mathbf{2HBr}\,(g)$

(b) $\mathbf{CH_4}(g) + \mathbf{I_2}(g) \longrightarrow \mathbf{CH_3I}\,(g) + \mathbf{HI}\,(g)$

(c) $\mathbf{C_2H_4}(g) + \mathbf{3O_2}(g) \longrightarrow \mathbf{2CO_2}(g) + \mathbf{2H_2O}\,(g)$

89.

Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $\mathbf{Cl_2}(g) + \mathbf{3F_2}(g) \longrightarrow \mathbf{2ClF_3}(g)$

(b) $\mathbf{H_2C=CH_2}(g) + \mathbf{H_2}(g) \longrightarrow \mathbf{H_3CCH_3}(g)$

(c) $\mathbf{2C_2H_6}(g) + \mathbf{7O_2}(g) \longrightarrow \mathbf{4CO_2}(g) + \mathbf{6H_2O}\,(g)$

90.

Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

(a) Use the bond energy found in Table 9.3 and Table 9.4 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)

(b) Use the enthalpy of reaction and the bond energies for H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

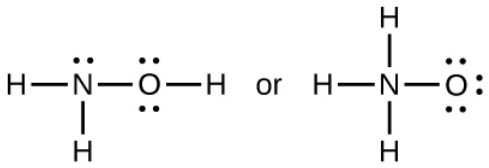
$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \qquad \Delta H^\circ_{rxn} = -184.7 \text{ kJ/mol}$$

91.

Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

92.

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



93.

How does the bond energy of HCl(g) differ from the standard enthalpy of formation of HCl(g)?

94.

Using the standard enthalpy of formation data in Appendix G, show how the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

95.

Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

96.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

97.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

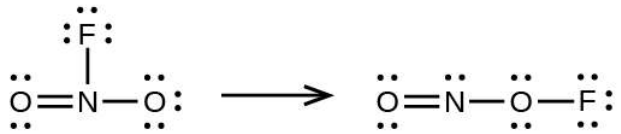
98.

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:



99.

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?



100.

Use principles of atomic structure to answer each of the following:[4]

(a) The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.

(b) The lattice energy of CaO(*s*) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.

(c) Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

(d) The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

101.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

102.

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

(a) MgO

(b) SrO

(c) KF

(d) CsF

(e) MgF_2

103.

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $\mathbf{M}(s) + \mathbf{X_2}(g) \longrightarrow \mathbf{MX_2}(s)$. For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

(a) a large radius vs. a small radius for M^{+2}

(b) a high ionization energy vs. a low ionization energy for M

(c) an increasing bond energy for the halogen

(d) a decreasing electron affinity for the halogen

(e) an increasing size of the anion formed by the halogen

104.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

105.

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^{+} have similar radii; O^{2-} and F^{-} have similar radii. Explain your choices.

(a) MgO or MgSe

(b) LiF or MgO

(c) Li_2O or LiCl

(d) Li_2Se or MgO

106.

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and

K^{+} have similar radii; S^{2-} and Cl^{-} have similar radii. Explain your choices.

(a) K_2O or Na_2O

(b) K_2S or BaS

(c) KCl or BaS

(d) BaS or $BaCl_2$

107.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) MgO

(b) SrO

(c) KF

(d) CsF

(e) MgF_2

108.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) K_2S

(b) K_2O

(c) CaS

(d) Cs_2S

(e) CaO

109.

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F

distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

Footnotes

- 4This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

This page titled 10.6: Exercises (Thermochemistry) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

10.6.1: Answers to Selected Exercises

1.

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

3.

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

5.

(a) 47.6 J/°C; 11.38 cal $°C^{-1}$; (b) 407 J/°C; 97.3 cal $°C^{-1}$

7.

1310 J; 313 cal

9.

7.15 °C

11.

(a) 0.390 J/g °C; (b) Copper is a likely candidate.

13.

We assume that the density of water is 1.0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7.47 kWh

15.

lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

17.

greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": $q_{rxn} = -(q_{solution} + q_{calorimeter})$; since both $q_{solution}$ and $q_{calorimeter}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

19.

The temperature of the coffee will drop 1 degree.

21.

5.7×10^2 kJ

23.

38.5 °C

25.

−2.2 kJ; The heat produced shows that the reaction is exothermic.

27.

1.4 kJ

29.

22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

31.

11.7 kJ

33.

30%

35.

0.24 g

37.

1.4×10^2 Calories

39.

The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH.

41.

25 kJ mol^{-1}

43.

81 kJ mol^{-1}

45.

5204.4 kJ

47.

1.83×10^{-2} mol

49.

–802 kJ mol^{-1}

51.

15.5 kJ/ºC

53.

7.43 g

55.

Yes.

57.

459.6 kJ

59.

−494 kJ/mol

61.

44.01 kJ/mol

63.

−394 kJ

65.

265 kJ

67.

90.3 kJ/mol

69.

(a) −1615.0 kJ mol^{-1}; (b) −484.3 kJ mol^{-1}; (c) 164.2 kJ; (d) −232.1 kJ

71.

−54.04 kJ mol^{-1}

73.

−2660 kJ mol^{-1}

75.

–66.4 kJ

77.

−122.8 kJ

79.

3.7 kg

81.

On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.

83.

−88.2 kJ

85.

(a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$; (b) 330 L air; (c) −104.5 kJ mol^{-1}; (d) 75.4 °C

88.

(a) −114 kJ;
(b) 30 kJ;
(c) −1055 kJ

91.

The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

92.

The greater bond energy is in the figure on the left. It is the more stable form.

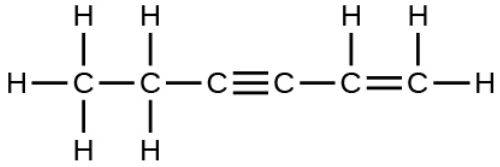
94.

$$\begin{aligned}
&HCl(g) \longrightarrow \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) && \Delta\text{msubsupmsubsup} = -\Delta\text{msubsupmsubsup}\\
&\tfrac{1}{2}H_2(g) \longrightarrow H(g) && \Delta\text{msubsupmsubsup} = \Delta\text{msubsupmsubsup}\\
&\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g) && \Delta\text{msubsupmsubsup} = \Delta\text{msubsupmsubsup}\\
&\overline{HCl(g) \longrightarrow H(g) + Cl(g)} && \Delta\text{msubsupmsubsup} = \Delta\text{msubsupmsubsup} + \Delta\text{msubsupmsubsup} + \Delta\text{msubsupmsubsup}\\
&D_{HCl} = \Delta\text{msubsupmsubsup} && = \Delta\text{msubsupmsubsup} + \Delta\text{msubsupmsubsup} + \Delta\text{msubsupmsubsup}\\
& && = -(-92.307\,kJ) + 217.97\,kJ + 121.3\,kJ\\
& && = 431.6\,kJ
\end{aligned}$$

96.

The S–F bond in SF_4 is stronger.

98.



The C–C single bonds are longest.

100.

(a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower $n = 3$ level, which is much smaller in radius. (b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. (d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

102.

(d)

104.

4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

106.

(a) Na_2O; Na^+ has a smaller radius than K^+; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

108.

(e)

This page titled 10.6.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

10.7: Exercises (Thermodynamics)

1.

What is a spontaneous reaction?

2.

What is a nonspontaneous reaction?

3.

Indicate whether the following processes are spontaneous or nonspontaneous.

(a) Liquid water freezing at a temperature below its freezing point

(b) Liquid water freezing at a temperature above its freezing point

(c) The combustion of gasoline

(d) A ball thrown into the air

(e) A raindrop falling to the ground

(f) Iron rusting in a moist atmosphere

4.

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5.

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

6.

In Figure 12.8 all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

7.

In Figure 12.8 all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution (b) to distribution (d).

8.

How does the process described in the previous item relate to the system shown in Figure 12.4?

9.

Consider a system similar to the one in Figure 12.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

10.

Consider the system shown in Figure 12.9. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

11.

Consider the system shown in Figure 12.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

12.

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $H_2(g)$, $HBrO_4(g)$, $HBr(g)$

(b) $H_2O(l)$, $H_2O(g)$, $H_2O(s)$

(c) $He(g)$, $Cl_2(g)$, $P_4(g)$

13.

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

14.

Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$$\mathbf{I_2}(s) \longrightarrow \mathbf{I_2}(g)$$

$$\mathbf{I_2}(s) \longrightarrow \mathbf{I_2}(l)$$

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15.

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $C_2H_5OH(l)$ or $C_3H_7OH(l)$

(b) $C_2H_5OH(l)$ or $C_2H_5OH(g)$

(c) $2H(g)$ or $H(g)$

16.

Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.

(b) Exhaled breath forms fog on a cold morning.

(c) Snow melts.

17.

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $\mathbf{Na^+}(aq) + \mathbf{Cl^-}(aq) \longrightarrow \mathbf{NaCl}(s)$

(b) $\mathbf{2Fe}(s) + \frac{3}{2}\mathbf{O_2}(g) \longrightarrow \mathbf{Fe_2O_2}(s)$

(c) $\mathbf{2C_6H_{14}}(l) + \mathbf{19O_2}(g) \longrightarrow \mathbf{14H_2O}(g) + \mathbf{12CO_2}(g)$

18.

Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19.

Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

20.

What is the difference between ΔS and $\Delta S°$ for a chemical change?

21.

Calculate $\Delta S°$ for the following changes.

(a) $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(g)$

(b) $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l)$

(c) $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}(g)$

(d) $\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$

(e) $2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(l)$

(f) $2\mathrm{HCl}(g) + \mathrm{Pb}(s) \longrightarrow \mathrm{PbCl_2}(s) + \mathrm{H_2}(g)$

(g) $\mathrm{Zn}(s) + \mathrm{CuSO_4}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(s)$

22.

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under the standard conditions to give gaseous carbon dioxide and liquid water.

23.

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

24.

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $\mathrm{Fe_2O_3}(s) + 2\mathrm{Al}(s) \longrightarrow \mathrm{Al_2O_3}(s) + 2\mathrm{Fe}(s)$. Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25.

Using the relevant $S°$ values listed in Appendix G, calculate $\Delta S°_{298}$ for the following changes:

(a) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g)$

(b) $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

26.

From the following information, determine $\Delta S°$ for the following:

$\mathrm{N}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) \qquad \Delta S° = ?$

$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta S° = 24.8\ J/K$

$N_2(g) \longrightarrow 2N(g) \qquad \Delta S° = 115.0\ J/K$

$O_2(g) \longrightarrow 2O(g) \qquad \Delta S° = 117.0\ J/K$

27.

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.
$S°_{NaCl(s)} = 72.11 \frac{J}{mol \cdot K} \qquad S°_{NaCl(l)} = 95.06 \frac{J}{mol \cdot K} \qquad \Delta H°_{fusion} = 27.95\ kJ/mol$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

28.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

(a) $MnO_2(s) \longrightarrow Mn(s) + O_2(g)$

(b) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$

(c) $Cu(s) + S(g) \longrightarrow CuS(s)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

(e) $CH_4(g) + O_2(g) \longrightarrow C(s,\ graphite) + 2H_2O(g)$

(f) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

29.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

(a) $C(s,\ graphite) + O_2(g) \longrightarrow CO_2(g)$

(b) $O_2(g) + N_2(g) \longrightarrow 2NO(g)$

(c) $2Cu(s) + S(g) \longrightarrow Cu_2S(s)$

(d) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$

(e) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

(f) $CaSO_4 \cdot 2H_2O(s) \longrightarrow CaSO_4(s) + 2H_2O(g)$

30.

What is the difference between ΔG and $\Delta G°$ for a chemical change?

31.

A reaction has $\Delta H°$ = 100 kJ/mol and $\Delta S° = 250\ J/mol \cdot K$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

32.

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

33.

Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these

conditions.

(a) $\mathrm{MnO_2}(s) \longrightarrow \mathrm{Mn}(s) + \mathrm{O_2}(g)$

(b) $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{HBr}(g)$

(c) $\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{CuS}(s)$

(d) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g)$

(e) $\mathrm{CH_4}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{C}(s,\ \text{graphite}) + 2\mathrm{H_2O}(g)$

(f) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

34.

Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $\mathrm{C}(s,\ \text{graphite}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$

(b) $\mathrm{O_2}(g) + \mathrm{N_2}(g) \longrightarrow 2\mathrm{NO}(g)$

(c) $2\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{Cu_2S}(s)$

(d) $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$

(e) $\mathrm{Fe_2O_3}(s) + 3\mathrm{CO}(g) \longrightarrow 2\mathrm{Fe}(s) + 3\mathrm{CO_2}(g)$

(f) $\mathrm{CaSO_4{\cdot}2H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\mathrm{H_2O}(g)$

35.

Given:

$\mathrm{P_4}(s) + 5\mathrm{O_2}(g) \longrightarrow \mathrm{P_4O_{10}}(s) \qquad \Delta G^\circ = -2697.0\ \mathrm{kJ/mol}$

$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(g) \qquad \Delta G^\circ = -457.18\ \mathrm{kJ/mol}$

$6\mathrm{H_2O}(g) + \mathrm{P_4O_{10}}(s) \longrightarrow 4\mathrm{H_3PO_4}(l) \qquad \Delta G^\circ = -428.66\ \mathrm{kJ/mol}$

(a) Determine the standard free energy of formation, ΔG_f°, for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

36.

Is the formation of ozone ($\mathrm{O_3}(g)$) from oxygen ($\mathrm{O_2}(g)$) spontaneous at room temperature under standard state conditions?

37.

Consider the decomposition of red mercury(II) oxide under standard state conditions.

$2\mathrm{HgO}(s,\ \text{red}) \longrightarrow 2\mathrm{Hg}(l) + \mathrm{O_2}(g)$

(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

38.

Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

(a) Ammonia: $2\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\mathrm{H_2}(g)$

(b) Diborane: $\mathrm{B_2H_6}(g) \longrightarrow 2\mathrm{B}(g) + 3\mathrm{H_2}(g)$

(c) Hydrazine: $\mathrm{N_2H_4}(g) \longrightarrow \mathrm{N_2}(g) + 2\mathrm{H_2}(g)$

(d) Hydrogen peroxide: $H_2O_2(l) \longrightarrow H_2O(g) + \frac{1}{2}O_2(g)$

39.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	T = 2000 °C	$K_p = 4.1 \times 10^{-4}$
(b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$	T = 400 °C	$K_p = 50.0$
(c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$	T = 980 °C	$K_p = 1.67$
(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	T = 900 °C	$K_p = 1.04$
(e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$	T = 25 °C	$K_p = 7.2 \times 10^{-4}$
(f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$	T = 25 °C	$K_p = 3.3 \times 10^{-13}$

40.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $Cl_2(g) + Br_2(g) \longrightarrow 2BrCl(g)$	T = 25 °C	$K_p = 4.7 \times 10^{-2}$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	T = 500 °C	$K_p = 48.2$
(c) $H_2O(l) \rightleftharpoons H_2O(g)$	T = 60 °C	$K_p = 0.196$
(d) $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$	T = 550 °C	$K_p = 4.90 \times 10^2$
(e) $CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3^+(aq) + OH^-(aq)$	T = 25 °C	$K_p = 4.4 \times 10^{-4}$
(f) $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2I^-(aq)$	T = 25 °C	$K_p = 8.7 \times 10^{-9}$

41.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$	$\Delta G° = -9.2$ kJ
(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$	$\Delta G° = 7.3$ kJ
(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$	$\Delta G° = -79$ kJ
(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$	$\Delta G° = -1.6$ kJ
(e) $SnCl_4(l) \longrightarrow SnCl_4(l)$	$\Delta G° = 8.0$ kJ

42.

Determine $\Delta G°$ for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$SbCl_5(g) \longrightarrow SbCl_3(g) + Cl_2(g)$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:

$Cl_2(g) \longrightarrow 2Cl(g)$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

43.

Given that the ΔG_f° for $Pb^{2+}(aq)$ and $Cl^-(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

44.

Determine the standard free energy change, ΔG_f°, for the formation of $S^{2-}(aq)$ given that the ΔG_f° for $Ag^+(aq)$ and $Ag_2S(s)$ are 77.1 kJ/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

45.

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

46.

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \qquad \Delta G° = 8.58\ \mathrm{kJ}$

(a) Is the evaporation of water under standard thermodynamic conditions spontaneous?

(b) Determine the equilibrium constant, K_P, for this physical process.

(c) By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, $P_{\mathrm{H_2O}}$, is 0.011 atm.

(d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of $P_{\mathrm{H_2O}}$ in the air?

47.

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$\mathrm{Glu} + \mathrm{ATP} \longrightarrow \mathrm{G6P} + \mathrm{ADP} \qquad \Delta G° = -17\ \mathrm{kJ}$

In this process, ATP becomes ADP summarized by the following equation:

$\mathrm{ATP} \longrightarrow \mathrm{ADP} \qquad \Delta G° = -30\ \mathrm{kJ}$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$\mathrm{Glu} \longrightarrow \mathrm{G6P} \qquad \Delta G° = ?$

48.

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$\mathrm{G6P} \rightleftharpoons \mathrm{F6P} \qquad \Delta G° = 1.7\ \mathrm{kJ}$

(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?

(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

49.

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

(a) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g)$

(b) $\mathrm{HCl}(g) + \mathrm{NH_3}(g) \longrightarrow \mathrm{NH_4Cl}(s)$

(c) $(\mathrm{NH_4})_2\mathrm{Cr_2O_7}(s) \longrightarrow \mathrm{Cr_2O_3}(s) + 4\mathrm{H_2O}(g) + \mathrm{N_2}(g)$

(d) $2\mathrm{Fe}(s) + 3\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$

50.

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

51.

An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

$$Cu_2S(s) \longrightarrow Cu(s) + S(s)$$

(a) Determine $\Delta G°$ for the decomposition of $Cu_2S(s)$.

(b) The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine $\Delta G°$ for the process.

(c) The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

52.

What happens to $\Delta G°$ (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $S(s) + O_2(g) \longrightarrow SO_2(g)$

(b) $2SO_2(g) + O_2(g) \longrightarrow SO_3(g)$

(c) $HgO(s) \longrightarrow Hg(l) + O_2(g)$

This page titled 10.7: Exercises (Thermodynamics) is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Jesse Crandall.

10.7.1: Answers to Selected Exercises

1.

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

3.

(a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

5.

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

7.

There are four initial microstates and four final microstates.

$\Delta S = k \ln \frac{W_f}{W_i} = 1.38 \times 10^{-}\text{msup}\,\text{J/K} \times \ln \frac{4}{4} =$

9.

The probability for all the particles to be on one side is $\frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

11.

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$\Delta S = k \ln \left(\frac{W_f}{W_i}\right) = 1.38 \times 10^{-}\text{msup}\,\text{J/K} \times \ln \left(\frac{4}{1}\right) = 1.91 \times 10^{-}\text{msup}\,\text{J/}$

13.

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

15.

(a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $C_2H_5OH(g)$ as it is in the gaseous state. (c) $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

17.

(a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

19.

$C_6H_6(l) + 7.5O_2(g) \longrightarrow 3H_2O(g) + 6CO_2(g)$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

21.

(a) 107 J/K; (b) −86.4 J/K; (c) 133.2 J/K; (d) 118.8 J/K; (e) −326.6 J/K; (f) −171.9 J/K; (g) −7.2 J/K

23.

100.6 J/K

25.

(a) −198.1 J/K; (b) −348.9 J/K

27.

As $\Delta S_{univ} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

29.

(a) 2.86 J/K; (b) 24.8 J/K; (c) −113.2 J/K; (d) −24.7 J/K; (e) 15.5 J/K; (f) 290.0 J/K

31.

The reaction is nonspontaneous at room temperature.
Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

33.

(a) 465.1 kJ nonspontaneous; (b) −106.86 kJ spontaneous; (c) −291.9 kJ spontaneous; (d) −83.4 kJ spontaneous; (e) −406.7 kJ spontaneous; (f) −154.3 kJ spontaneous

35.

(a) The standard free energy of formation is –1124.3 kJ/mol. (b) The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

37.

(a) The reaction is nonspontaneous; (b) Above 566 °C the process is spontaneous.

39.

(a) 1.5×10^2 kJ; (b) −21.9 kJ; (c) −5.34 kJ; (d) −0.383 kJ; (e) 18 kJ; (f) 71 kJ

41.

(a) $K = 41$; (b) $K = 0.053$; (c) $K = 6.9 \times 10^{13}$; (d) $K = 1.9$; (e) $K = 0.04$

42.

(a) 22.1 kJ;
(b) 98.9 kJ/mol

44.

90 kJ/mol

46.

(a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; (b) $K_p = 0.031$; (c) The evaporation of water is spontaneous; (d) P_{H_2O} must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

48.

(a) Nonspontaneous as $\Delta G° > 0$; (b) $\Delta G° = \Delta$msupmsup$+RT \ln Q$, $\Delta G = 1.7 \times 10^3 + \left(8.314 \times 310 \times \ln \frac{28}{120}\right) = -2.1$ kJ. The forward reaction to produce F6P is spontaneous under these conditions.

50.

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

52.

(a) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of K. $\Delta G°$ therefore becomes more negative.
(b) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of K. $\Delta G°$ therefore becomes more negative.
(c) Increasing P_{O_2} will shift the equilibrium the reactants, which decreases the value of K. $\Delta G°$ therefore becomes more positive.

This page titled 10.7.1: Answers to Selected Exercises is shared under a not declared license and was authored, remixed, and/or curated by Jesse Crandall.

Appendix: Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
aluminum			
Al(s)	0	0	28.3
Al(g)	324.4	285.7	164.54
Al_2O_3(s)	–1676	–1582	50.92
AlF_3(s)	–1510.4	–1425	66.5
$AlCl_3$(s)	–704.2	–628.8	110.67
$AlCl_3 \cdot 6H_2O$(s)	–2691.57	–2269.40	376.56
Al_2S_3(s)	–724.0	–492.4	116.9
$Al_2(SO_4)_3$(s)	–3445.06	–3506.61	239.32
antimony			
Sb(s)	0	0	45.69
Sb(g)	262.34	222.17	180.16
Sb_4O_6(s)	–1440.55	–1268.17	220.92
$SbCl_3$(g)	–313.8	–301.2	337.80
$SbCl_5$(g)	–394.34	–334.29	401.94
Sb_2S_3(s)	–174.89	–173.64	182.00
$SbCl_3$(s)	–382.17	–323.72	184.10
SbOCl(s)	–374.0	—	—
arsenic			
As(s)	0	0	35.1
As(g)	302.5	261.0	174.21
As_4(g)	143.9	92.4	314
As_4O_6(s)	–1313.94	–1152.52	214.22
As_2O_5(s)	–924.87	–782.41	105.44
$AsCl_3$(g)	–261.50	–248.95	327.06
As_2S_3(s)	–169.03	–168.62	163.59
AsH_3(g)	66.44	68.93	222.78
H_3AsO_4(s)	–906.3	—	—
barium			
Ba(s)	0	0	62.5
Ba(g)	180	146	170.24
BaO(s)	–548.0	–520.3	72.1

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$BaCl_2(s)$	–855.0	–806.7	123.7
$BaSO_4(s)$	–1473.2	–1362.3	132.2
beryllium			
$Be(s)$	0	0	9.50
$Be(g)$	324.3	286.6	136.27
$BeO(s)$	–609.4	–580.1	13.8
bismuth			
$Bi(s)$	0	0	56.74
$Bi(g)$	207.1	168.2	187.00
$Bi_2O_3(s)$	–573.88	–493.7	151.5
$BiCl_3(s)$	–379.07	–315.06	176.98
$Bi_2S_3(s)$	–143.1	–140.6	200.4
boron			
$B(s)$	0	0	5.86
$B(g)$	565.0	521.0	153.4
$B_2O_3(s)$	–1273.5	–1194.3	53.97
$B_2H_6(g)$	36.4	87.6	232.1
$H_3BO_3(s)$	–1094.33	–968.92	88.83
$BF_3(g)$	–1136.0	–1119.4	254.4
$BCl_3(g)$	–403.8	–388.7	290.1
$B_3N_3H_6(l)$	–540.99	–392.79	199.58
$HBO_2(s)$	–794.25	–723.41	37.66
bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.142	245.5
$Br(g)$	111.88	82.429	175.0
$BrF_3(g)$	–255.60	–229.45	292.42
$HBr(g)$	–36.3	–53.43	198.7
cadmium			
$Cd(s)$	0	0	51.76
$Cd(g)$	112.01	77.41	167.75
$CdO(s)$	–258.2	–228.4	54.8

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$CdCl_2(s)$	–391.5	–343.9	115.3
$CdSO_4(s)$	–933.3	–822.7	123.0
$CdS(s)$	–161.9	–156.5	64.9
calcium			
$Ca(s)$	0	0	41.6
$Ca(g)$	178.2	144.3	154.88
$CaO(s)$	–634.9	–603.3	38.1
$Ca(OH)_2(s)$	–985.2	–897.5	83.4
$CaSO_4(s)$	–1434.5	–1322.0	106.5
$CaSO_4{\cdot}2H_2O(s)$	–2022.63	–1797.45	194.14
$CaCO_3(s)$ (calcite)	–1220.0	–1081.4	110.0
$CaSO_3{\cdot}H_2O(s)$	–1752.68	–1555.19	184.10
carbon			
$C(s)$ (graphite)	0	0	5.740
$C(s)$ (diamond)	1.89	2.90	2.38
$C(g)$	716.681	671.2	158.1
$CO(g)$	–110.52	–137.15	197.7
$CO_2(g)$	–393.51	–394.36	213.8
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$CoO(s)$	–237.9	–214.2	52.97

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
$CuO(s)$	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
$CuS(s)$	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
$F(g)$	79.4	62.3	158.8
$F_2O(g)$	24.7	41.9	247.43
$HF(g)$	–273.3	–275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
$H(g)$	217.97	203.26	114.7
$H_2O(l)$	–285.83	–237.1	70.0
$H_2O(g)$	–241.82	–228.59	188.8
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(g)$	–136.3	–105.6	232.7
$HF(g)$	–273.3	–275.4	173.8
$HCl(g)$	–92.307	–95.299	186.9
$HBr(g)$	–36.3	–53.43	198.7
$HI(g)$	26.48	1.70	206.59
$H_2S(g)$	–20.6	–33.4	205.8
$H_2Se(g)$	29.7	15.9	219.0
iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.3	260.7

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
I(g)	106.84	70.2	180.8
IF(g)	95.65	–118.49	236.06
ICl(g)	17.78	–5.44	247.44
IBr(g)	40.84	3.72	258.66
$IF_7(g)$	–943.91	–818.39	346.44
HI(g)	26.48	1.70	206.59
iron			
Fe(s)	0	0	27.3
Fe(g)	416.3	370.7	180.5
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(CO)_5(l)$	–774.04	–705.42	338.07
$Fe(CO)_5(g)$	–733.87	–697.26	445.18
$FeCl_2(s)$	–341.79	–302.30	117.95
$FeCl_3(s)$	–399.49	–334.00	142.3
FeO(s)	–272.0	–255.2	60.75
$Fe(OH)_2(s)$	–569.0	–486.5	88.
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
FeS(s)	–100.0	–100.4	60.29
$Fe_3C(s)$	25.10	20.08	104.60
lead			
Pb(s)	0	0	64.81
Pb(g)	195.2	162.	175.4
PbO(s) (yellow)	–217.32	–187.89	68.70
PbO(s) (red)	–218.99	–188.93	66.5
$Pb(OH)_2(s)$	–515.9	—	—
PbS(s)	–100.4	–98.7	91.2
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
Li(s)	0	0	29.1

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Li(g)	159.3	126.6	138.8
LiH(s)	–90.5	–68.3	20.0
Li(OH)(s)	–487.5	–441.5	42.8
LiF(s)	–616.0	–587.5	35.7
Li_2CO_3(s)	–1216.04	–1132.19	90.17
manganese			
Mn(s)	0	0	32.0
Mn(g)	280.7	238.5	173.7
MnO(s)	–385.2	–362.9	59.71
MnO_2(s)	–520.03	–465.1	53.05
Mn_2O_3(s)	–958.97	–881.15	110.46
Mn_3O_4(s)	–1378.83	–1283.23	155.64
mercury			
Hg(l)	0	0	75.9
Hg(g)	61.4	31.8	175.0
HgO(s) (red)	–90.83	–58.5	70.29
HgO(s) (yellow)	–90.46	–58.43	71.13
$HgCl_2$(s)	–224.3	–178.6	146.0
Hg_2Cl_2(s)	–265.4	–210.7	191.6
HgS(s) (red)	–58.16	–50.6	82.4
HgS(s) (black)	–53.56	–47.70	88.28
$HgSO_4$(s)	–707.51	–594.13	0.00
nitrogen			
N_2(g)	0	0	191.6
N(g)	472.704	455.5	153.3
NO(g)	90.25	87.6	210.8
NO_2(g)	33.2	51.30	240.1
N_2O(g)	81.6	103.7	220.0
N_2O_3(g)	83.72	139.41	312.17
N_2O_4(g)	11.1	99.8	304.4
N_2O_5(g)	11.3	115.1	355.7
NH_3(g)	–45.9	–16.5	192.8

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$HPO_3(s)$	–948.5	—	—
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
$K(s)$	0	0	64.7

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
K(*g*)	89.0	60.5	160.3
KF(*s*)	–576.27	–537.75	66.57
KCl(*s*)	–436.5	–408.5	82.6
silicon			
Si(*s*)	0	0	18.8
Si(*g*)	450.0	405.5	168.0
SiO_2(*s*)	–910.7	–856.3	41.5
SiH_4(*g*)	34.3	56.9	204.6
H_2SiO_3(*s*)	–1188.67	–1092.44	133.89
H_4SiO_4(*s*)	–1481.14	–1333.02	192.46
SiF_4(*g*)	–1615.0	–1572.8	282.8
$SiCl_4$(*l*)	–687.0	–619.8	239.7
$SiCl_4$(*g*)	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
Ag(*s*)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89
Ag_2O(*s*)	–31.05	–11.20	121.3
AgCl(*s*)	–127.0	–109.8	96.3
Ag_2S(*s*)	–32.6	–40.7	144.0
sodium			
Na(*s*)	0	0	51.3
Na(*g*)	107.5	77.0	153.7
Na_2O(*s*)	–414.2	–375.5	75.1
NaCl(*s*)	–411.2	–384.1	72.1
sulfur			
S_8(*s*) (rhombic)	0	0	256.8
S(*g*)	278.81	238.25	167.82
SO_2(*g*)	–296.83	–300.1	248.2
SO_3(*g*)	–395.72	–371.06	256.76
H_2S(*g*)	–20.6	–33.4	205.8

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$H_2SO_4(l)$	–813.989	690.00	156.90
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5
SnO(s)	–285.8	–256.9	56.5
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(l)$	–511.3	–440.1	258.6
$SnCl_4(g)$	–471.5	–432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
$TiO_2(s)$	–944.0	–888.8	50.6
$TiCl_4(l)$	–804.2	–737.2	252.4
$TiCl_4(g)$	–763.2	–726.3	353.2
tungsten			
W(s)	0	0	32.6
W(g)	849.4	807.1	174.0
$WO_3(s)$	–842.9	–764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(g)	130.73	95.14	160.98

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
ZnO(*s*)	–350.5	–320.5	43.7
$ZnCl_2$(*s*)	–415.1	–369.43	111.5
ZnS(*s*)	–206.0	–201.3	57.7
$ZnSO_4$(*s*)	–982.8	–871.5	110.5
$ZnCO_3$(*s*)	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

Index

A

absolute zero
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
accuracy
2.2: Measurement Uncertainty, Accuracy, and Precision
acid ionization
9.4: Brønsted-Lowry Acids and Bases
acidic
9.5: pH and pOH
actinide
2.4: The Periodic Table
actual yield
7.4: Reaction Yields
adhesive force
4.4.1: Extra-Properties of Liquids
alkali metal
2.4: The Periodic Table
alkaline earth metal
2.4: The Periodic Table
alloy
5.4: The Dissolution Process
alpha decay
2.7: Radioactive Decay
alpha particle
2.6.2: Extra-Evolution of Atomic Theory
Amonton's law
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
amphiprotic
9.4: Brønsted-Lowry Acids and Bases
amphoteric
9.4: Brønsted-Lowry Acids and Bases
angular momentum quantum number
3.3.1: Extra-Orbital Origin and Shape
anion
2.6: Atomic Structure and Symbolism
aqueous solution
5.3: Molarity
atmosphere
6.1: Gas Pressure
atom
1.2: Phases and Classification of Matter
atomic mass
2.6: Atomic Structure and Symbolism
atomic mass unit
2.6: Atomic Structure and Symbolism
atomic number
2.6: Atomic Structure and Symbolism
atomic orbital
3.3.1: Extra-Orbital Origin and Shape
Aufbau principle
3.3: Electronic Structure of Atoms (Electron Configurations)
autoionization
9.4: Brønsted-Lowry Acids and Bases
average rate
8.1: Chemical Reaction Rates
avogadro's law
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
Avogadro's number
5.1: Formula Mass and the Mole Concept
axial position
4.2: Molecular Structure and Polarity

B

balanced equation
7.1: Writing and Balancing Chemical Equations
bar
6.1: Gas Pressure
barometer
6.1: Gas Pressure
base ionization
9.4: Brønsted-Lowry Acids and Bases
basic
9.5: pH and pOH
becquerel (unit)
2.7.3: Extra-Biological Effects of Radiation
beta decay
2.7: Radioactive Decay
binary acid
3.2: Chemical Nomenclature
binary compound
3.2: Chemical Nomenclature
bomb calorimeter
10.2: Calorimetry
bond angle
4.2: Molecular Structure and Polarity
bond dipole moment
4.2: Molecular Structure and Polarity
bond distance
4.2: Molecular Structure and Polarity
bond length
3.5: Covalent Bonding
Boyle's law
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
buffer
9.4.1: Buffers
buffer capacity
9.4.1: Buffers

C

calorie
10.1: Energy Basics
calorimeter
10.2: Calorimetry
calorimetry
10.2: Calorimetry
capillary action
4.4.1: Extra-Properties of Liquids
catalyst
8.2: Factors Affecting Reaction Rates
cation
2.6: Atomic Structure and Symbolism
chalcogen
2.4: The Periodic Table
Charles's Law
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
chemical change
1.3: Physical and Chemical Properties
chemical equation
7.1: Writing and Balancing Chemical Equations
chemical property
1.3: Physical and Chemical Properties
chemical symbol
2.6: Atomic Structure and Symbolism
chemical thermodynamics
10.3: Enthalpy
Chemotherapy
2.7.2: Extra-Uses of Radioisotopes
coefficient
7.1: Writing and Balancing Chemical Equations
cohesive force
4.4.1: Extra-Properties of Liquids
combustion reaction
7.2: Classifying Chemical Reactions
complete ionic equation
7.1: Writing and Balancing Chemical Equations
compound
1.2: Phases and Classification of Matter
concentrated
5.3: Molarity
concentration
5.3: Molarity
conjugate acid
9.4: Brønsted-Lowry Acids and Bases
conjugate base
9.4: Brønsted-Lowry Acids and Bases
conversion factors
2.3: Mathematical Treatment of Measurement Results
core electron
3.3: Electronic Structure of Atoms (Electron Configurations)
covalent bond
3.1: Molecular and Ionic Compounds
3.5: Covalent Bonding
covalent compound
3.1: Molecular and Ionic Compounds
curie (unit)
2.7.3: Extra-Biological Effects of Radiation

D

d orbital
3.3.1: Extra-Orbital Origin and Shape
Dalton unit
2.6: Atomic Structure and Symbolism
Dalton's Atomic Theory
2.6.1: Extra-Early Atomic Theory
Dalton's Law of Partial Pressure
6.2.1: Molar Mass of a Gas and Dalton's Law
daughter nuclide
2.7: Radioactive Decay
dilution
5.3: Molarity
dimensional analysis
2.3: Mathematical Treatment of Measurement Results
dipole moment
4.2: Molecular Structure and Polarity

Dispersion
4.4: Intermolecular Forces
dissociation
5.5: Electrolytes
dissolved
5.3: Molarity
double bond
4.1: Lewis Symbols and Structures

E

electrolyte
5.5: Electrolytes
Electron
2.6.2: Extra-Evolution of Atomic Theory
electron capture
2.7: Radioactive Decay
electron configuration
3.3: Electronic Structure of Atoms (Electron Configurations)
electron density
3.3.1: Extra-Orbital Origin and Shape
electronegativity
3.5: Covalent Bonding
element
1.2: Phases and Classification of Matter
empirical formula
2.5: Chemical Formulas
empirical formula mass
5.2: Determining Empirical and Molecular Formulas
endothermic process
10.1: Energy Basics
energy
10.1: Energy Basics
enthalpy
10.3: Enthalpy
enthalpy change
10.3: Enthalpy
entropy
10.4.1.1: Entropy
equatorial position
4.2: Molecular Structure and Polarity
equilibrium
9.1: Chemical Equilibria
exact number
2.2: Measurement Uncertainty, Accuracy, and Precision
excess reactant
7.4: Reaction Yields
exothermic process
10.1: Energy Basics
expansion work
10.3: Enthalpy
extensive property
1.3: Physical and Chemical Properties
external beam radiation therapy
2.7.2: Extra-Uses of Radioisotopes

F

f orbital
3.3.1: Extra-Orbital Origin and Shape
Fahrenheit
2.3: Mathematical Treatment of Measurement Results
first law of thermodynamics
10.3: Enthalpy
formal charge
4.1.1: Extra-Formal Charges and Resonance
formula mass
5.1: Formula Mass and the Mole Concept
free radical
4.1: Lewis Symbols and Structures
fundamental unit of charge
2.6: Atomic Structure and Symbolism

G

gamma emission
2.7: Radioactive Decay
gas
1.2: Phases and Classification of Matter
Geiger counter
2.7.3: Extra-Biological Effects of Radiation
Gibbs free energy
10.5: Free Energy
goiter
2.6: Atomic Structure and Symbolism
gray (unit)
2.7.3: Extra-Biological Effects of Radiation
group
2.4: The Periodic Table

H

halogen
2.4: The Periodic Table
heat
10.1: Energy Basics
heat capacity
10.1: Energy Basics
Heisenberg uncertainty principle
3.3.1: Extra-Orbital Origin and Shape
Hess's law
10.3: Enthalpy
heterogeneous catalyst
8.4: Catalysis
heterogeneous mixture
1.2: Phases and Classification of Matter
homogeneous catalyst
8.4: Catalysis
homogeneous mixture
1.2: Phases and Classification of Matter
Hund's rule
3.3: Electronic Structure of Atoms (Electron Configurations)
hybrid orbital
4.3: Hybrid Atomic Orbitals
hybridization
4.3: Hybrid Atomic Orbitals
hydrocarbon
10.3: Enthalpy
hydrogen bonding
4.4: Intermolecular Forces
hydrostatic pressure
6.1: Gas Pressure
hypervalent molecule
4.1: Lewis Symbols and Structures

I

ideal gas
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
ideal gas constant
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
ideal gas law
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
ideal solution
5.4: The Dissolution Process
induced dipole
4.4: Intermolecular Forces
inert gas
2.4: The Periodic Table
inert pair effect
3.4: Ionic Bonding
initial rate
8.1: Chemical Reaction Rates
inner transition metal
2.4: The Periodic Table
instantaneous dipole
4.4: Intermolecular Forces
instantaneous rate
8.1: Chemical Reaction Rates
intensive property
1.3: Physical and Chemical Properties
intermolecular force
4.4: Intermolecular Forces
internal energy
10.3: Enthalpy
internal radiation therapy
2.7.2: Extra-Uses of Radioisotopes
ion
2.6: Atomic Structure and Symbolism
ionic bond
3.1: Molecular and Ionic Compounds
3.4: Ionic Bonding
ionic compound
3.1: Molecular and Ionic Compounds
ionizing radiation
2.7.3: Extra-Biological Effects of Radiation
isomers
2.5: Chemical Formulas
isotope
2.6.2: Extra-Evolution of Atomic Theory

J

joule
10.1: Energy Basics

K

kinetic energy
10.1: Energy Basics
kinetic molecular theory
6.2.2: The Kinetic-Molecular Theory

L

lanthanide
2.4: The Periodic Table
law of conservation of matter
1.2: Phases and Classification of Matter

law of constant composition
2.6.1: Extra-Early Atomic Theory
law of definite proportions
2.6.1: Extra-Early Atomic Theory
law of multiple proportions
2.6.1: Extra-Early Atomic Theory
Le Chatelier's principle
9.3: Shifting Equilibria- Le Châtelier’s Principle
Lewis structure
4.1: Lewis Symbols and Structures
Lewis symbol
4.1: Lewis Symbols and Structures
limiting reactant
7.4: Reaction Yields
linear
4.2: Molecular Structure and Polarity
liquid
1.2: Phases and Classification of Matter
lone pair
4.1: Lewis Symbols and Structures

M

magnetic quantum number
3.3.1: Extra-Orbital Origin and Shape
manometer
6.1: Gas Pressure
mass
1.2: Phases and Classification of Matter
mass number
2.6: Atomic Structure and Symbolism
metal
2.4: The Periodic Table
metalloid
2.4: The Periodic Table
Method of Initial Rates
8.3: Rate Laws
microstates
10.4.1.1: Entropy
millicurie (unit)
2.7.3: Extra-Biological Effects of Radiation
mixture
1.2: Phases and Classification of Matter
molar mass
5.1: Formula Mass and the Mole Concept
molarity
5.3: Molarity
mole
5.1: Formula Mass and the Mole Concept
mole fraction
6.2.1: Molar Mass of a Gas and Dalton's Law
molecular compound
3.1: Molecular and Ionic Compounds
molecular equation
7.1: Writing and Balancing Chemical Equations
molecular formula
2.5: Chemical Formulas
Molecular Structure
4.1.1: Extra-Formal Charges and Resonance
4.2: Molecular Structure and Polarity
molecule
1.2: Phases and Classification of Matter
monatomic ion
3.1: Molecular and Ionic Compounds

N

net ionic equation
7.1: Writing and Balancing Chemical Equations
neutral
9.5: pH and pOH
neutron
2.6.2: Extra-Evolution of Atomic Theory
noble gas
2.4: The Periodic Table
nomenclature
3.2: Chemical Nomenclature
nonelectrolyte
5.5: Electrolytes
nonionizing radiation
2.7.3: Extra-Biological Effects of Radiation
nonmetal
2.4: The Periodic Table
nonpolar covalent bond
3.5: Covalent Bonding
nonspontaneous process
10.4.1: Spontaneity
nucleus
2.6.2: Extra-Evolution of Atomic Theory
nutritional calorie
10.2: Calorimetry

O

octahedral
4.2: Molecular Structure and Polarity
octet rule
4.1: Lewis Symbols and Structures
orbital diagram
3.3: Electronic Structure of Atoms (Electron Configurations)
overall reaction order
8.3: Rate Laws
oxidation
7.2: Classifying Chemical Reactions
oxidizing agent
7.2: Classifying Chemical Reactions
oxyacid
3.2: Chemical Nomenclature
oxyanion
3.1: Molecular and Ionic Compounds

P

p orbital
3.3.1: Extra-Orbital Origin and Shape
parent nuclide
2.7: Radioactive Decay
partial pressure
6.2.1: Molar Mass of a Gas and Dalton's Law
Pascal
6.1: Gas Pressure
Pauli exclusion principle
3.3.1: Extra-Orbital Origin and Shape
percent composition
5.2: Determining Empirical and Molecular Formulas
percent yield
7.4: Reaction Yields
period
2.4: The Periodic Table
periodic law
2.4: The Periodic Table
periodic table
2.4: The Periodic Table
pH
9.5: pH and pOH
physical change
1.3: Physical and Chemical Properties
physical property
1.3: Physical and Chemical Properties
plasma
1.2: Phases and Classification of Matter
pnictogen
2.4: The Periodic Table
pOH
9.5: pH and pOH
polar covalent bond
3.5: Covalent Bonding
polar molecule
4.2: Molecular Structure and Polarity
Polarizability
4.4: Intermolecular Forces
polyatomic ion
3.1: Molecular and Ionic Compounds
position of equilibrium
9.3: Shifting Equilibria- Le Châtelier’s Principle
positron emission
2.7: Radioactive Decay
potential energy
10.1: Energy Basics
pounds per square inch
6.1: Gas Pressure
precipitate
7.2: Classifying Chemical Reactions
precipitation reaction
7.2: Classifying Chemical Reactions
precision
2.2: Measurement Uncertainty, Accuracy, and Precision
pressure
6.1: Gas Pressure
principal quantum number
3.3.1: Extra-Orbital Origin and Shape
product
7.1: Writing and Balancing Chemical Equations
proton
2.6.2: Extra-Evolution of Atomic Theory
PSI (Unit)
6.1: Gas Pressure
pure covalent bond
3.5: Covalent Bonding
pure substance
1.2: Phases and Classification of Matter

Q

quantum mechanics
3.3.1: Extra-Orbital Origin and Shape

R

radiation absorbed dose
2.7.3: Extra-Biological Effects of Radiation
radiation dosimeter
2.7.3: Extra-Biological Effects of Radiation

radiation therapy
2.7.2: Extra-Uses of Radioisotopes
radioactive decay
2.7: Radioactive Decay
radioactive decay series
2.7: Radioactive Decay
radioactive tracer
2.7.2: Extra-Uses of Radioisotopes
radiocarbon dating
2.7: Radioactive Decay
radiometric dating
2.7: Radioactive Decay
rate constant
8.3: Rate Laws
rate expression
8.1: Chemical Reaction Rates
rate law
8.3: Rate Laws
rate of reaction
8.1: Chemical Reaction Rates
reactant
7.1: Writing and Balancing Chemical Equations
reaction order
8.3: Rate Laws
reduction
7.2: Classifying Chemical Reactions
relative biological effectiveness
2.7.3: Extra-Biological Effects of Radiation
representative element
2.4: The Periodic Table
resonance
4.1.1: Extra-Formal Charges and Resonance
4.3.1: Extra-Multiple Bonds
resonance forms
4.1.1: Extra-Formal Charges and Resonance
resonance hybrid
4.1.1: Extra-Formal Charges and Resonance
Reversible Process
10.4.1.1: Entropy
reversible reaction
9.1: Chemical Equilibria
roentgen equivalent man
2.7.3: Extra-Biological Effects of Radiation
root mean square velocity
6.2.2: The Kinetic-Molecular Theory
rounding
2.2: Measurement Uncertainty, Accuracy, and Precision

S

s orbital
3.3.1: Extra-Orbital Origin and Shape
scintillation counter
2.7.3: Extra-Biological Effects of Radiation
second law of thermodynamics
10.4.1.2: The Second and Third Laws of Thermodynamics
series
2.4: The Periodic Table
shell
3.3.1: Extra-Orbital Origin and Shape
sievert (unit)
2.7.3: Extra-Biological Effects of Radiation
significant figures
2.2: Measurement Uncertainty, Accuracy, and Precision
single bond
4.1: Lewis Symbols and Structures
solid
1.2: Phases and Classification of Matter
solute
5.3: Molarity
solvation
5.4: The Dissolution Process
solvent
5.3: Molarity
sp hybrid orbital
4.3: Hybrid Atomic Orbitals
sp2 hybrid orbital
4.3: Hybrid Atomic Orbitals
sp3 hybrid orbital
4.3: Hybrid Atomic Orbitals
sp3d hybrid orbital
4.3: Hybrid Atomic Orbitals
sp3d2 hybrid orbital
4.3: Hybrid Atomic Orbitals
spatial isomers
2.5: Chemical Formulas
specific heat capacity
10.1: Energy Basics
spectator ion
7.1: Writing and Balancing Chemical Equations
spin quantum number
3.3.1: Extra-Orbital Origin and Shape
spontaneous change
10.4.1: Spontaneity
spontaneous process
5.4: The Dissolution Process
standard conditions of temperature and pressure
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
standard enthalpy of combustion
10.3: Enthalpy
standard enthalpy of formation
10.3: Enthalpy
standard entropy
10.4.1.2: The Second and Third Laws of Thermodynamics
standard entropy change
10.4.1.2: The Second and Third Laws of Thermodynamics
standard free energy change
10.5: Free Energy
standard free energy of formation
10.5: Free Energy
standard molar volume
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
standard state
10.3: Enthalpy
state function
10.3: Enthalpy
stoichiometric factor
7.3: Reaction Stoichiometry
stoichiometry
7.3: Reaction Stoichiometry
STP
6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
stress
9.3: Shifting Equilibria- Le Châtelier's Principle
strong electrolyte
5.5: Electrolytes
structural formula
2.5: Chemical Formulas
structural isomers
2.5: Chemical Formulas
subshell
3.3.1: Extra-Orbital Origin and Shape
surface tension
4.4.1: Extra-Properties of Liquids
surroundings
10.2: Calorimetry
system
10.2: Calorimetry

T

temperature
10.1: Energy Basics
tetrahedral
4.2: Molecular Structure and Polarity
theoretical yield
7.4: Reaction Yields
thermal energy
10.1: Energy Basics
thermochemistry
10.1: Energy Basics
Third Law of Thermodynamics
10.4.1.2: The Second and Third Laws of Thermodynamics
titration curve
9.4.2: Acid-Base Titrations
Torr
6.1: Gas Pressure
transition metal
2.4: The Periodic Table
trigonal bipyramidal
4.2: Molecular Structure and Polarity
trigonal planar
4.2: Molecular Structure and Polarity
triple bond
4.1: Lewis Symbols and Structures

U

uncertainty
2.2: Measurement Uncertainty, Accuracy, and Precision
unified atomic mass unit
2.6: Atomic Structure and Symbolism

V

valence electrons
3.3: Electronic Structure of Atoms (Electron Configurations)
valence shell
3.3: Electronic Structure of Atoms (Electron Configurations)
valence shell electron pair repulsion theory
4.2: Molecular Structure and Polarity

van der Waals force
4.4: Intermolecular Forces
vapor pressure of water
6.2.1: Molar Mass of a Gas and Dalton's Law
viscosity
4.4.1: Extra-Properties of Liquids
VSEPR
4.2: Molecular Structure and Polarity
W
wavefunction
3.3.1: Extra-Orbital Origin and Shape
weak electrolyte
5.5: Electrolytes
weight
1.2: Phases and Classification of Matter
work
10.1: Energy Basics

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: CHM 120: Survey of General Chemistry (Crandall)

Webpages: 113

All licenses found:

- CC BY 4.0: 65.5% (74 pages)
- Undeclared: 34.5% (39 pages)

By Page

- CHM 120: Survey of General Chemistry (Crandall) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Introduction to Chemistry - *Undeclared*
    - 1.1: Introduction - *Undeclared*
    - 1.2: Phases and Classification of Matter - *CC BY 4.0*
    - 1.3: Physical and Chemical Properties - *CC BY 4.0*
    - 1.4: Exercises - *CC BY 4.0*
      - 1.4.1: Answers to Selected Exercises - *Undeclared*
  - 2: Measurements and the Periodic Table - *Undeclared*
    - 2.1: Measurements - *CC BY 4.0*
    - 2.2: Measurement Uncertainty, Accuracy, and Precision - *CC BY 4.0*
    - 2.3: Mathematical Treatment of Measurement Results - *CC BY 4.0*
    - 2.4: The Periodic Table - *CC BY 4.0*
    - 2.5: Chemical Formulas - *CC BY 4.0*
    - 2.6: Atomic Structure and Symbolism - *CC BY 4.0*
      - 2.6.1: Extra-Early Atomic Theory - *CC BY 4.0*
      - 2.6.2: Extra-Evolution of Atomic Theory - *CC BY 4.0*
    - 2.7: Radioactive Decay - *CC BY 4.0*
      - 2.7.1: Nuclear Equations - *CC BY 4.0*
      - 2.7.2: Extra-Uses of Radioisotopes - *CC BY 4.0*
      - 2.7.3: Extra-Biological Effects of Radiation - *CC BY 4.0*
    - 2.8: Exercises - *CC BY 4.0*
      - 2.8.1: Answers to Selected Exercises - *Undeclared*
    - 2.9: Exercises for Nuclear Reactions - *CC BY 4.0*
      - 2.9.1: Answers to Exercises for Nuclear Reactions - *Undeclared*
  - 3: Ions, Compounds, and Molecules - *Undeclared*
    - 3.1: Molecular and Ionic Compounds - *CC BY 4.0*
    - 3.2: Chemical Nomenclature - *CC BY 4.0*
    - 3.3: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
      - 3.3.1: Extra-Orbital Origin and Shape - *CC BY 4.0*
    - 3.4: Ionic Bonding - *CC BY 4.0*
    - 3.5: Covalent Bonding - *CC BY 4.0*
    - 3.6: Exercises - *CC BY 4.0*
      - 3.6.1: Answers to Selected Exercises - *Undeclared*
  - 4: Lewis Structures; Geometry and Polarity of Molecules - *Undeclared*
    - 4.1: Lewis Symbols and Structures - *CC BY 4.0*
      - 4.1.1: Extra-Formal Charges and Resonance - *CC BY 4.0*
    - 4.2: Molecular Structure and Polarity - *CC BY 4.0*
    - 4.3: Hybrid Atomic Orbitals - *CC BY 4.0*
      - 4.3.1: Extra-Multiple Bonds - *CC BY 4.0*
    - 4.4: Intermolecular Forces - *CC BY 4.0*
      - 4.4.1: Extra-Properties of Liquids - *CC BY 4.0*
    - 4.5: Exercises (Lewis Structures) - *CC BY 4.0*
      - 4.5.1: Answers to Selected Exercises - *Undeclared*
    - 4.6: Exercises (Intermolecular Forces) - *CC BY 4.0*
      - 4.6.1: Answers to Selected Exercises - *Undeclared*
  - 5: Moles, Molar Mass, Concentration, and Solutions - *Undeclared*
    - 5.1: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 5.2: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 5.3: Molarity - *CC BY 4.0*
    - 5.4: The Dissolution Process - *CC BY 4.0*
    - 5.5: Electrolytes - *CC BY 4.0*

- 5.6: Exercises (Solutions and Concentrations) - *CC BY 4.0*
  - 5.6.1: Answers to Selected Exercises - *Undeclared*
- 5.7: Exercises (Moles and Chemical Formulas) - *CC BY 4.0*
  - 5.7.1: Answers to Selected Exercises (Moles and Chemical Formulas) - *Undeclared*

6: Gases and the Ideal Gas Law - *Undeclared*
- 6.1: Gas Pressure - *CC BY 4.0*
- 6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law - *CC BY 4.0*
  - 6.2.1: Molar Mass of a Gas and Dalton's Law - *CC BY 4.0*
  - 6.2.2: The Kinetic-Molecular Theory - *CC BY 4.0*
- 6.3: Exercises - *CC BY 4.0*
  - 6.3.1: Answers to Selected Exercises - *Undeclared*

7: Chemical Reactions and Stoichiometry - *Undeclared*
- 7.1: Writing and Balancing Chemical Equations - *CC BY 4.0*
- 7.2: Classifying Chemical Reactions - *CC BY 4.0*
- 7.3: Reaction Stoichiometry - *CC BY 4.0*
- 7.4: Reaction Yields - *CC BY 4.0*
- 7.5: Exercises - *CC BY 4.0*
  - 7.5.1: Answers to Selected Exercises - *Undeclared*

8: Kinetics- Rates of Chemical Reactions - *Undeclared*
- 8.1: Chemical Reaction Rates - *CC BY 4.0*
- 8.2: Factors Affecting Reaction Rates - *CC BY 4.0*
- 8.3: Rate Laws - *CC BY 4.0*
- 8.4: Catalysis - *CC BY 4.0*
- 8.5: Exercises - *CC BY 4.0*
  - 8.5.1: Answers to selected Exercises - *Undeclared*

9: Equilibrium and Acid Base Chemistry - *Undeclared*
- 9.1: Chemical Equilibria - *CC BY 4.0*
- 9.2: Equilibrium Constants - *CC BY 4.0*
- 9.3: Shifting Equilibria- Le Châtelier's Principle - *CC BY 4.0*
- 9.4: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
  - 9.4.1: Buffers - *CC BY 4.0*
  - 9.4.2: Acid-Base Titrations - *CC BY 4.0*
- 9.5: pH and pOH - *CC BY 4.0*
- 9.6: Exercises (Equilibrium) - *CC BY 4.0*
  - 9.6.1: Chapter 13 - *Undeclared*
- 9.7: Exercises (Acid-Base) - *CC BY 4.0*
  - 9.7.1: Answers to Selected Exercises - *Undeclared*

10: Thermochemistry and Thermodynamics - *Undeclared*
- 10.1: Energy Basics - *CC BY 4.0*
- 10.2: Calorimetry - *CC BY 4.0*
- 10.3: Enthalpy - *CC BY 4.0*
- 10.4: Thermodynamics - *Undeclared*
  - 10.4.1: Spontaneity - *CC BY 4.0*
    - 10.4.1.1: Entropy - *CC BY 4.0*
    - 10.4.1.2: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
  - 10.4.2: New Page - *Undeclared*
- 10.5: Free Energy - *CC BY 4.0*
- 10.6: Exercises (Thermochemistry) - *CC BY 4.0*
  - 10.6.1: Answers to Selected Exercises - *Undeclared*
- 10.7: Exercises (Thermodynamics) - *CC BY 4.0*
  - 10.7.1: Answers to Selected Exercises - *Undeclared*

Back Matter - *Undeclared*
- Appendix: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*

Detailed Licensing

Overview

Title: CHM 120: Survey of General Chemistry (Crandall)

Webpages: 113

All licenses found:

- CC BY 4.0: 65.5% (74 pages)
- Undeclared: 34.5% (39 pages)

By Page

- CHM 120: Survey of General Chemistry (Crandall) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Introduction to Chemistry - *Undeclared*
    - 1.1: Introduction - *Undeclared*
    - 1.2: Phases and Classification of Matter - *CC BY 4.0*
    - 1.3: Physical and Chemical Properties - *CC BY 4.0*
    - 1.4: Exercises - *CC BY 4.0*
      - 1.4.1: Answers to Selected Exercises - *Undeclared*
  - 2: Measurements and the Periodic Table - *Undeclared*
    - 2.1: Measurements - *CC BY 4.0*
    - 2.2: Measurement Uncertainty, Accuracy, and Precision - *CC BY 4.0*
    - 2.3: Mathematical Treatment of Measurement Results - *CC BY 4.0*
    - 2.4: The Periodic Table - *CC BY 4.0*
    - 2.5: Chemical Formulas - *CC BY 4.0*
    - 2.6: Atomic Structure and Symbolism - *CC BY 4.0*
      - 2.6.1: Extra-Early Atomic Theory - *CC BY 4.0*
      - 2.6.2: Extra-Evolution of Atomic Theory - *CC BY 4.0*
    - 2.7: Radioactive Decay - *CC BY 4.0*
      - 2.7.1: Nuclear Equations - *CC BY 4.0*
      - 2.7.2: Extra-Uses of Radioisotopes - *CC BY 4.0*
      - 2.7.3: Extra-Biological Effects of Radiation - *CC BY 4.0*
    - 2.8: Exercises - *CC BY 4.0*
      - 2.8.1: Answers to Selected Exercises - *Undeclared*
    - 2.9: Exercises for Nuclear Reactions - *CC BY 4.0*
      - 2.9.1: Answers to Exercises for Nuclear Reactions - *Undeclared*
  - 3: Ions, Compounds, and Molecules - *Undeclared*
    - 3.1: Molecular and Ionic Compounds - *CC BY 4.0*
    - 3.2: Chemical Nomenclature - *CC BY 4.0*
    - 3.3: Electronic Structure of Atoms (Electron Configurations) - *CC BY 4.0*
      - 3.3.1: Extra-Orbital Origin and Shape - *CC BY 4.0*
    - 3.4: Ionic Bonding - *CC BY 4.0*
    - 3.5: Covalent Bonding - *CC BY 4.0*
    - 3.6: Exercises - *CC BY 4.0*
      - 3.6.1: Answers to Selected Exercises - *Undeclared*
  - 4: Lewis Structures; Geometry and Polarity of Molecules - *Undeclared*
    - 4.1: Lewis Symbols and Structures - *CC BY 4.0*
      - 4.1.1: Extra-Formal Charges and Resonance - *CC BY 4.0*
    - 4.2: Molecular Structure and Polarity - *CC BY 4.0*
    - 4.3: Hybrid Atomic Orbitals - *CC BY 4.0*
      - 4.3.1: Extra-Multiple Bonds - *CC BY 4.0*
    - 4.4: Intermolecular Forces - *CC BY 4.0*
      - 4.4.1: Extra-Properties of Liquids - *CC BY 4.0*
    - 4.5: Exercises (Lewis Structures) - *CC BY 4.0*
      - 4.5.1: Answers to Selected Exercises - *Undeclared*
    - 4.6: Exercises (Intermolecular Forces) - *CC BY 4.0*
      - 4.6.1: Answers to Selected Exercises - *Undeclared*
  - 5: Moles, Molar Mass, Concentration, and Solutions - *Undeclared*
    - 5.1: Formula Mass and the Mole Concept - *CC BY 4.0*
    - 5.2: Determining Empirical and Molecular Formulas - *CC BY 4.0*
    - 5.3: Molarity - *CC BY 4.0*
    - 5.4: The Dissolution Process - *CC BY 4.0*
    - 5.5: Electrolytes - *CC BY 4.0*

- 5.6: Exercises (Solutions and Concentrations) - *CC BY 4.0*
  - 5.6.1: Answers to Selected Exercises - *Undeclared*
- 5.7: Exercises (Moles and Chemical Formulas) - *CC BY 4.0*
  - 5.7.1: Answers to Selected Exercises (Moles and Chemical Formulas) - *Undeclared*

6: Gases and the Ideal Gas Law - *Undeclared*
- 6.1: Gas Pressure - *CC BY 4.0*
- 6.2: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law - *CC BY 4.0*
  - 6.2.1: Molar Mass of a Gas and Dalton's Law - *CC BY 4.0*
  - 6.2.2: The Kinetic-Molecular Theory - *CC BY 4.0*
- 6.3: Exercises - *CC BY 4.0*
  - 6.3.1: Answers to Selected Exercises - *Undeclared*

7: Chemical Reactions and Stoichiometry - *Undeclared*
- 7.1: Writing and Balancing Chemical Equations - *CC BY 4.0*
- 7.2: Classifying Chemical Reactions - *CC BY 4.0*
- 7.3: Reaction Stoichiometry - *CC BY 4.0*
- 7.4: Reaction Yields - *CC BY 4.0*
- 7.5: Exercises - *CC BY 4.0*
  - 7.5.1: Answers to Selected Exercises - *Undeclared*

8: Kinetics- Rates of Chemical Reactions - *Undeclared*
- 8.1: Chemical Reaction Rates - *CC BY 4.0*
- 8.2: Factors Affecting Reaction Rates - *CC BY 4.0*
- 8.3: Rate Laws - *CC BY 4.0*
- 8.4: Catalysis - *CC BY 4.0*
- 8.5: Exercises - *CC BY 4.0*
  - 8.5.1: Answers to selected Exercises - *Undeclared*

9: Equilibrium and Acid Base Chemistry - *Undeclared*
- 9.1: Chemical Equilibria - *CC BY 4.0*
- 9.2: Equilibrium Constants - *CC BY 4.0*
- 9.3: Shifting Equilibria- Le Châtelier's Principle - *CC BY 4.0*
- 9.4: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
  - 9.4.1: Buffers - *CC BY 4.0*
  - 9.4.2: Acid-Base Titrations - *CC BY 4.0*
- 9.5: pH and pOH - *CC BY 4.0*
- 9.6: Exercises (Equilibrium) - *CC BY 4.0*
  - 9.6.1: Chapter 13 - *Undeclared*
- 9.7: Exercises (Acid-Base) - *CC BY 4.0*
  - 9.7.1: Answers to Selected Exercises - *Undeclared*

10: Thermochemistry and Thermodynamics - *Undeclared*
- 10.1: Energy Basics - *CC BY 4.0*
- 10.2: Calorimetry - *CC BY 4.0*
- 10.3: Enthalpy - *CC BY 4.0*
- 10.4: Thermodynamics - *Undeclared*
  - 10.4.1: Spontaneity - *CC BY 4.0*
    - 10.4.1.1: Entropy - *CC BY 4.0*
    - 10.4.1.2: The Second and Third Laws of Thermodynamics - *CC BY 4.0*
  - 10.4.2: New Page - *Undeclared*
- 10.5: Free Energy - *CC BY 4.0*
- 10.6: Exercises (Thermochemistry) - *CC BY 4.0*
  - 10.6.1: Answers to Selected Exercises - *Undeclared*
- 10.7: Exercises (Thermodynamics) - *CC BY 4.0*
  - 10.7.1: Answers to Selected Exercises - *Undeclared*

Back Matter - *Undeclared*
- Appendix: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
- Index - *Undeclared*
- Glossary - *Undeclared*
- Detailed Licensing - *Undeclared*
- Detailed Licensing - *Undeclared*